

SNOW AS AN ACCUMULATOR OF
ACID POLLUTANTS IN COLORADO

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ABSTRACT

SNOW AS AN ACCUMULATOR OF ACID
POLLUTANTS IN COLORADO

Water quality of snow was investigated from August 1981, to March, 1983, in the high alpine watersheds of Colorado. The primary objective of this study was to assess the impact of ski areas on water quality as snow and to investigate mechanisms of acidification which contribute to the contamination of snow. Snow samples were obtained at six sites covering southern (Telluride), central (Vail, Keystone, Flat Tops Wilderness Area), and northern (Cameron Pass, Rabbit Ears Pass) Colorado. The pH was measured at all sites and acidity at the northern Colorado sites. Laboratory analyses of $\text{SO}_4^{=}$, NO_3^{-} , and Ca^{++} indicated greater contamination of snow in ski areas with pH values at or above the expected pH of 5.6 to 5.8. Calcium concentrations ranged from .18 to 12.52 mg/L and generally provided sufficient buffering to prevent acid snow from occurring. The source of calcium was thought to be local and anthropogenic, probably ash from fireplaces. Background pH values of snow in remote areas ranged from 4.4 to 5.5 and varied with different snowfall events. Acidity ranged from 14.1 to 27 mg CaCO_3 /L titrated to an endpoint of pH 8.3 and represented a possible hazard to unbuffered alpine lakes. Further research and future monitoring of selected sites is recommended.

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CHAPTER I

INTRODUCTION

During the past decade, the increased popularity of winter sports has concentrated people in a few high mountain valleys in the Rocky Mountain region. Most of the winter sports areas are located in complex topographic regions which limit the dispersion of pollutants emitted from the areas immediately around the sources (fireplaces in condominiums, auto parking lots, etc.). The air in these areas is, therefore, often quite contaminated.

The more important sink mechanisms for air pollutants in the Rocky Mountain region during winter are washout by snowfall, dry sedimentation of particulates onto the snowpack, and absorption of gases (Forland and Gjessing, 1974). For example, sulfate in the snowpack may result from the deposition of $\text{SO}_4^{=}$ particles and by absorption and solution of SO_2 in the snowpack with subsequent oxidation to $\text{SO}_4^{=}$. As a result, the snowpack in winter sports areas is believed to be quite acidic. At the time of spring thaw these acids may release heavy metals from the soil surface causing significant detrimental impacts on vegetation, soils, and the aquatic life of streams and lakes in the watersheds below the winter sports areas.

Previous Investigations of Regional Precipitation Quality

Few researchers have examined western precipitation quality. Lewis and Grant (1980) examined bulk precipitation (the composite of wet

plus dry) in the Como Creek watershed, Boulder County, Colorado, at an elevation of 2900 M and 6 Km east of the Continental Divide (See Figure 1). The area is considered wilderness and predominant airflow is from the northwest, a region of very sparse settlement. Upslope airflow does occasionally occur, drawing contaminants from the Denver Metropolitan area into the watershed. This is considered sporadic and not common in winter.

Two stations at Como Creek were sampled weekly over a three-year period. The stations did not have statistically different data ($P > .05$) and were thus averaged. The pH measurements were converted to hydrogen ion concentrations, averaged, then reconverted to pH. The analysis indicated an average pH of 5.43 with a standard error of 0.4 at the beginning of the study (Week 1, June, 1975). The pH declined at an average rate of 0.0053 units per week through the study. At the end of three years, the average pH had declined 0.80 units, from 5.43 to 4.63. The authors attribute the acidic conditions to an increase in NO_3^- combining with H^+ to form HNO_3 . Sulfate did not increase significantly ($P > .05$) and was not suspected of being a major contributor to the downward trend (Lewis and Grant, 1980).

Turk and Adams (1983) sampled lakes in the Flat Tops Wilderness Area of Colorado (See Figure 2) to determine alkalinity (quantitative capacity to react with a strong acid to a designated pH) and thus the buffering capacity of lakes in that region. The study concluded that there are lakes sensitive to acidification if precipitation in the area becomes as acidic as that of the northeastern United States. Alkalinity values as small as 3.5 mg CaCO_3/L occur in the higher elevation lakes. Most lakes at elevations of 3380 meters or greater

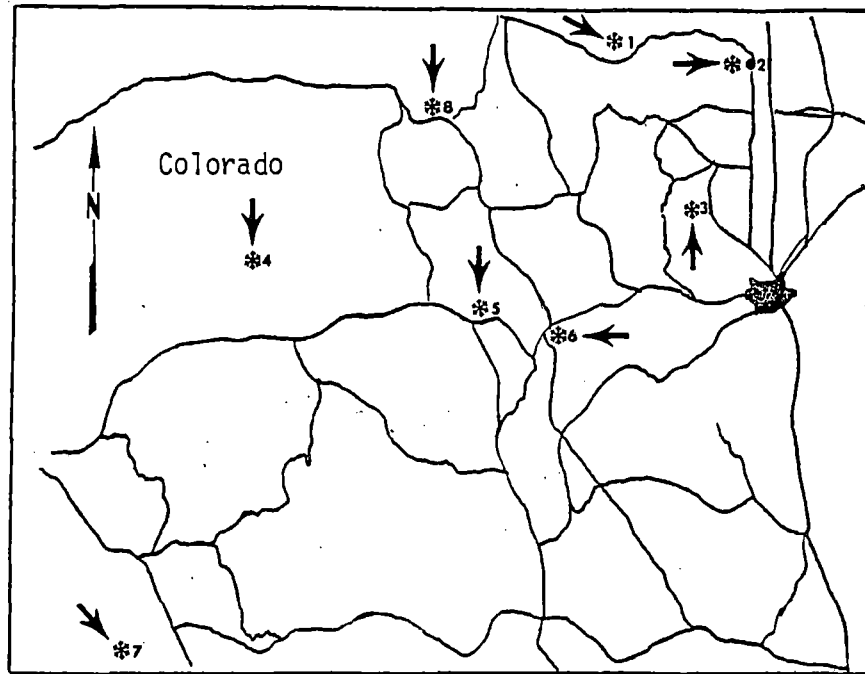


Figure 1. Map of research sites in Colorado.

- Key:
- 1) Cameron Pass
 - 2) Colorado State University, Fort Collins
 - 3) Como Creek Watershed
 - 4) Flat Tops Wilderness Area
 - 5) Vail
 - 6) Keystone
 - 7) Telluride
 - 8) Rabbit Ears Pass

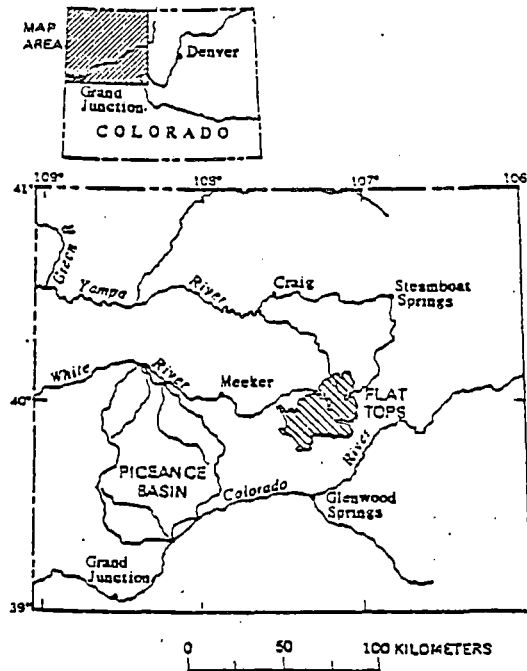


Figure 2. Location of Flat Tops Wilderness Area. (Turk and Adams, 1983).

are predicted to have alkalinity values of 10 mg CaCO_3/L or less. Three hundred seventy lakes, having a total surface area of about 157 hectares, were determined to be sensitive to acidification (Vimont, 1982).

Vimont (1982) investigated seven sites in Colorado (Wolf Creek Pass, Red Mountain Pass, Climax, Guanella Pass, Long Lake, Milner, and Rabbit Ears Pass) by digging snow pits at each site and measuring pH and conductivity with depth. Conclusions were based on multiple measurements in a single snow pit at each site and were:

- 1.) The range of pH values examined was 4.63 to 6.92.
- 2.) Approximately 20% of the snow samples were below a pH of 5.0, 60% were between a pH of 5.0 and 5.6, and 20% were above a pH of 5.6.
- 3.) Half of the samples from sites near local sources of acidic pollutants (coal fired power plants) had pH values less than 5.2.

Chemical Effects of Acid Snowmelt

Hagen and Langeland (1973) reported that, in winter, surface water in some oligo-dystrophic lakes in southern Norway (See Figure 3) differed physiochemically from what might be expected. This was attributed to pollution originating from sources in Europe and England and carried to Scandinavia via large air mass movements.

An indication of the source of pollution was obtained from the ice cover in Stemtjorn in November, 1970 (See Figure 4). In autumn the ice is depressed by the snow. Water soaks into the snow and freezes on the top and so the process continues. Thus the snow is trapped in between layers of ice until spring. In November, two layers

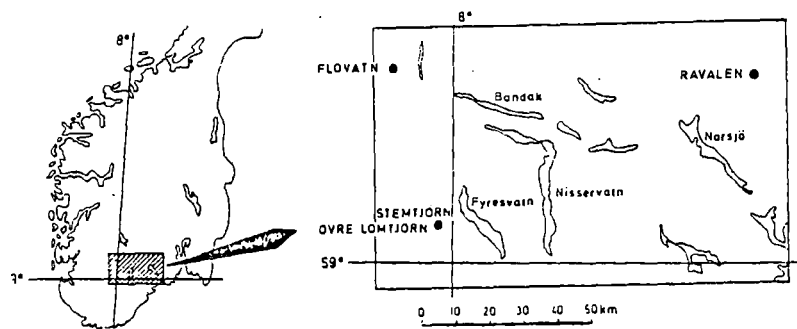


Figure 3. Southern Norway Region investigated by Hagen and Langeland (1978).

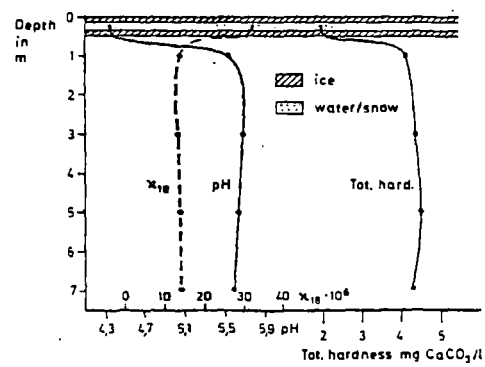


Figure 4. Physiochemical situation in Stemtjorn, November 29, 1970. (Hagen and Langeland, 1973) (electrical conductivity = $K_{18} \times 10^6$)

of ice were formed with a mixture of water and snow between them. As can be seen from Figure 4, this water differs considerably from the water in the lake itself with respect to conductivity, hardness, and acidity.

A consequence of this airborne pollution has been that many rivers and lakes in Norway and Sweden have shown a trend of increasing acidity with time (Anon, 1971; Oden, 1971; Henriksen, 1972; Snekvik, 1972). The types of lakes mentioned, oligotrophic and dystrophic lakes with lower buffering capacity, are very common in Scandinavia. Such lakes will be especially susceptible to acid precipitation, and severe pH-shocks may occur in the surface layers during the melting period in spring. The biological significance of such changes is uncertain, but they are most likely to have an influence upon the plankton, nekton, and littoral communities, rather than benthic organisms (Hagen and Langeland, 1973).

Acid Meltout

Of great concern to water quality hydrologists and pertinent to this study is the phenomena known as acid meltout.

Freshly deposited snow has a density of about 100 to 250 Kg/m³. With time the snowflakes become rounded in shape and break up into smaller grains while the strength and density of the snow increase due to transfer of water molecules through the vapor phase and volume diffusion through the ice. The rearrangement is particularly fast if the temperature is close to 0°C. Even at the beginning of the snow-melting period it seems likely that the dominant part of the impurities is found in a brine at the crystal surfaces, primarily at the grain boundaries (Siep, 1978).

Johannessen and Henriksen (1978) are among several researchers who have found, through laboratory and field experiments, that the first fractions of meltwater contain higher amounts of ions than the bulk snow. Lysimeters consisting of 56 cm long plastic tubes with 13 cm diameter were filled with more or less homogeneous snow. A 1.1 atm pressure of N_2 was applied to the top of the lysimeter, and a cooling mantle kept at 2.3 to 3.0°C. The meltwater was collected in 25 ml aliquots.

The concentration factor plotted in Figure 5 is defined as the concentration of a given ion in fraction i divided by the concentration in the bulk snow. In Figure 5, this factor is roughly 4 to 5 in the first fractions.

The melting conditions during this experiment are somewhat different from those found in nature. To reproduce field conditions somewhat more closely, the experiments have been repeated with the snow surrounded by well insulated walls and radiant energy supplied to the snow surface by a lamp. The concentration factors varies considerably with the rate of melting; values about 8 were obtained in a very slow melting process (Berg and Siep, unpublished results).

Johannessen and Henriksen (1978) have also carried out field experiments. Lysimeters consisting of a polyethylene cylinder (30 cm high and 53.5 cm in diameter) were buried in the ground in the fall, such that the top extended 3 cm above the ground surface, and were covered by a perforated polyethylene shutter. During the winter the snow accumulated on the top of the shutter and during periods of snowmelt the meltwater ran through the cylinder and was collected in

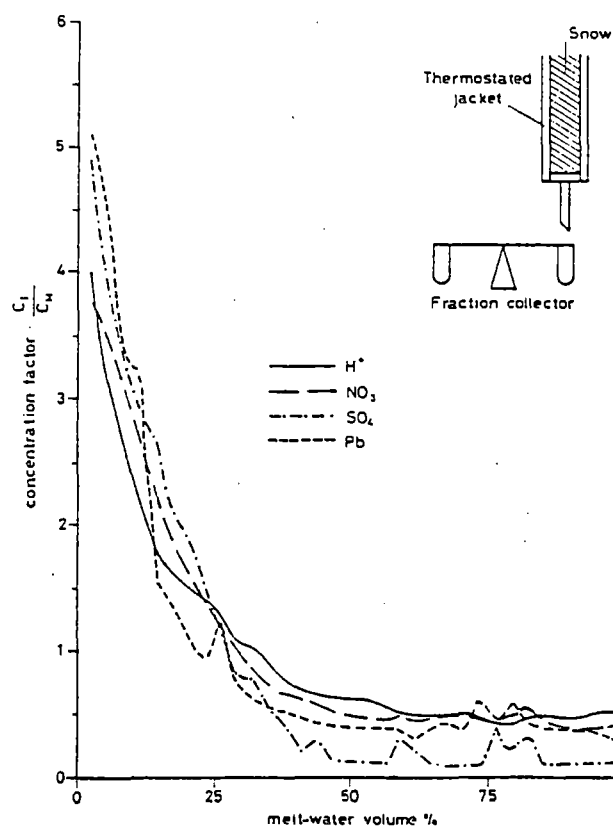


Figure 5. Concentration factors obtained in a melting experiment carried out in a laboratory. (Johannessen and Henriksen, 1978)

a polyethylene bottle. The concentration factors obtained in an experiment of this type are given in Figure 6.

The laboratory and field experiments indicate that 50 to 80 percent of the pollutants are released when the first 30 percent of the snow melts. The very first meltwater may have concentrations about 5 times the values found in bulk snow; in extreme cases the factors may reach ten (Siep, 1978). These high concentrations may be due to a freeze-concentration process during snow recrystallization and melting in which contaminants accumulate preferentially at the surfaces of ice particles (Johannessen and Henriksen, 1978). This phenomena of acid snowmelt greatly increases the potential impact of acid precipitation that occurs as snow.

Pollutant Deposition to the Snow Surface

In order to determine the magnitude of acidification of snow in Colorado, more must be known about the deposition of air pollutants onto snow, a complex and poorly understood phenomena. Three processes believed to be responsible for contaminating the snowpack are:

- 1.) Washout and rainout.
- 2.) Dry sedimentation of particles.
- 3.) Adsorption of gases.

Forland and Gjessing (1975) researched these processes in the Bergen Region of Norway (southwest coast). Dry snow was sampled from the ground at 46 locations just after a snowfall and three days later. Consistent and logical patterns for the two day were found for sulphate, magnesium, calcium, zinc, pH, and conductivity. The rate of dry deposition in the rural (including mountainous) areas was

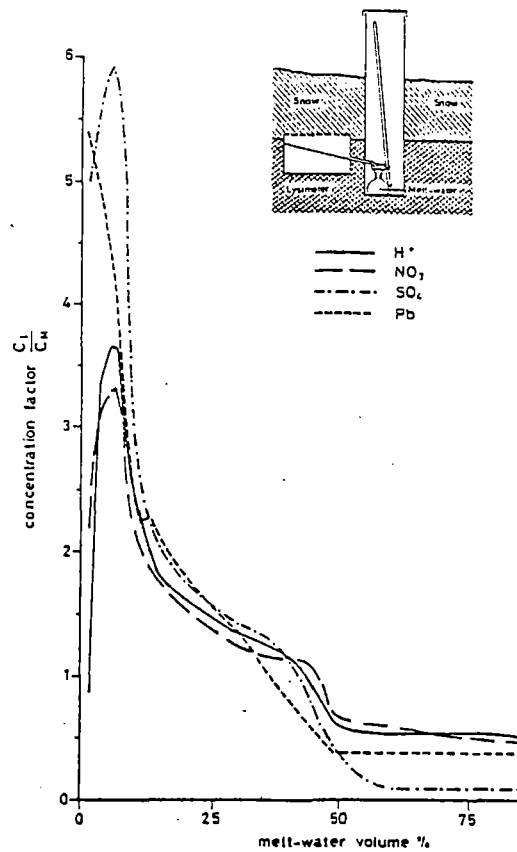


Figure 6. Concentration factors in meltwater obtained in a field lysimeter. (Johannessen and Henriksen, 1978)

significantly smaller than the rate of washout/rainout. In the city area these two rates were of the same magnitude.

If dry deposition and adsorption of gases at the surface were the predominant processes affecting snowpack purity, it would be reasonable to assume that the major part of the various pollutants should be concentrated at the surface and in the upper 2 to 3 cm of the snow samples, and that the lower snow layers would contain comparatively "clean" snow below. If, however, washout/rainout dominated, a layer of pollutants would occur in the first few centimeters of snow deposited in a given event, with subsequent snow being "cleaner". In actuality, a balance occurs between these three processes depending on a number of factors, including:

- 1.) The type of pollution, anthropogenic or natural.
- 2.) The physical characteristics of the sampling site.
- 3.) Atmospheric conditions.

Forland and Gjessing discovered that the rate of dry deposition of sulphate, magnesium, and calcium in the mountainous areas amounted to 13 to 15 percent of the city values. The washout/rainout process was of great importance in these rural areas. It was estimated to be 5 to 15 times higher than for the city, with the surrounding areas (non-city, non-mountain) in an intermediate position (Forland and Gjessing, 1975).

Impacts to Aquatic Organisms

When snowmelt pH drops below 5.6, a series of adverse effects begin to occur in wildlife. Some of the organisms most sensitive to pH change are aquatic and among these, trout are of particular concern for several reasons. Trout are economically significant throughout the world, especially in North America. Both commercial and recreational fisheries are valuable and, in most countries, a resource residents wish to protect. Unfortunately, trout are very intolerant of pH change. When a lake becomes acidified (to a level discussed later) the fry will suffer high mortality and survivors may be left in poor condition. The end result, if this cycle is not reversed, will be a decline or local extinction of the fry and smaller trout. Only the larger fish will survive and eventually will die without successfully reproducing. This will leave a lake devoid of an important species of game fish and may result in the dominance of less desirable and more acid-tolerant non-game fish, e.g., carp.

Rapid pH drops like those recorded by Hagen and Langeland are very likely to have hazardous effects on limnic organisms. Hatching of trout and salmon, for example, is known to be very sensitive to low pH values. Investigations by Bua and Snekvik (1972) showed that a minimum pH range for successful hatching of salmon was 5.0 to 5.5, of char 4.5 to 5.0, and of trout about 4.5. Trout had a 50% hatching at pH = 4.9. Furthermore, Snekvik (1969) reported the yolk stage as being most sensitive to low pH values. This stage in the trout may coincide with the snow melting in large parts of Scandinavia, and is

thus exposed to the most unfavorable water conditions possible. The potential spawning brooks in Fyresdal showed pH values down to 4.9 before snowmelting, thus, as might be expected, greatly reducing the success of eventual hatching (Hagen and Langeland, 1973). Biological investigations of fish life and zooplankton in Hagen and Langeland's study area revealed population decreases to levels which are considered poor for Norwegian oligotrophic lakes.

Research Objectives

The aforementioned investigations have dealt with pH measurements in alpine areas (Lewis and Grant, 1980), (Vimont, 1982); susceptibility of lakes to acidification (Turk and Adams, 1983); acid snow meltout phenomena (Siep, 1978), (Johannessen and Henriksen, 1978); deposition of acid pollutants (Forland and Gjessing, 1975); and acid snow phenomena affecting aquatic organisms (Hagen and Langeland, 1973), (Bua and Snekvik, 1972). This research project was designed to examine each of these subject areas (except for effects on wildlife) by conducting appropriate field and laboratory experimentation. Based on the concerns mentioned earlier, the following project objectives were established:

- a) To measure pH in the snowpack of two winter sports areas and at one or more remote sites at intervals throughout the accumulation period.
- b) To inventory emissions in the study areas and to relate the total acid pollutant buildup to one index of emission activity.
- c) To evaluate the magnitude of hazard posed by an acid buildup in the snowpack (if it exists) to water resources within the study areas.

As more information became available, additional important objectives were identified. These were:

- d) To determine the best sampling, measurement, and storage techniques for snow samples from the study areas.
- e) To determine if local meteorological conditions influence deposition of pollutants and thus pH.

- f) To design an experiment using snow obtained in a wilderness area to investigate the acid meltout phenomena.
- g) To determine the pH and acidity of snow in selected wilderness areas where the greatest vulnerability to lake acidification exists.

CHAPTER II

RESEARCH DESIGN AND METHODS

Investigations of snow contamination were performed by Dr. W. E. Marlatt, Professor of Air Resources and Bioclimatology, Colorado State University, during the 1981-1982 sampling period as part of a United States Forest Service sponsored research project. Further investigations were performed by Mr. Jeff Hepler, graduate student of Snow Hydrology and Andrew Boudreau, research assistant, at Colorado State University.

Two sites were initially selected for this study where distinct land use impacts were expected, and one site where little or no impact was foreseen. This chapter discusses the study area and reasons for its selection, the parameters measured, and sampling sites, and the techniques and equipment used to obtain each sample.

The Study Areas

The two "impacted" sites were Vail and Telluride, Colorado, located at elevations of 8,500 and 8,700 feet respectively (See Figure 1). Both are major ski areas and have experienced considerable growth in recent years. Associated with this growth has been an increase in air pollution. Poor air quality is particularly evident during heavy-use holiday periods, temperature inversions, or both.

One reason that Vail and Telluride were suspected of having possible acid snow conditions was the complex topography that surrounds

both communities. The dispersion of pollution is severely limited by terrain in Telluride and moderately restricted in Vail. Both locations are prone to air temperature inversions in which colder air is overlain by a warmer air layer, creating a stagnant condition with little vertical mixing. The studies at Vail and Telluride were designed to investigate possible correlations of local anthropogenic pollutant emissions with acidity found within the surrounding snowpack.

The Flat Tops Wilderness site is located in White River National Forest near the U.S.F.S. Ranger Station between Buford and Trapper Lakes at an elevation of 8100 feet (See Figure 7). It is considered free from local air and water pollution although some contamination due to long-range transport of pollutants from sources outside the immediate study area is possible. This location was used as a control site.

The three sampling locations at Telluride are located within the City of Telluride (See Figure 8) which is at the end of a horseshoe-shaped glacial valley. The hillsides rise steeply from the valley floor at 8,700 feet to above 12,000 feet on both sides of town and above the cirque wall two kilometers to the east. Frequent winter temperature inversions trap the emissions generated by Telluride's approximately 1,200 residents and the transient tourist/skier population. Emission levels vary in Telluride with the season and weather conditions (Groeneveld, 1977).

Telluride's three sites were designed Telluride East, West, and Center. All were located in areas which, by careful inspection, were thought to be representative of in-town atmospheric conditions and not heavily influenced by any single nearby pollution source.

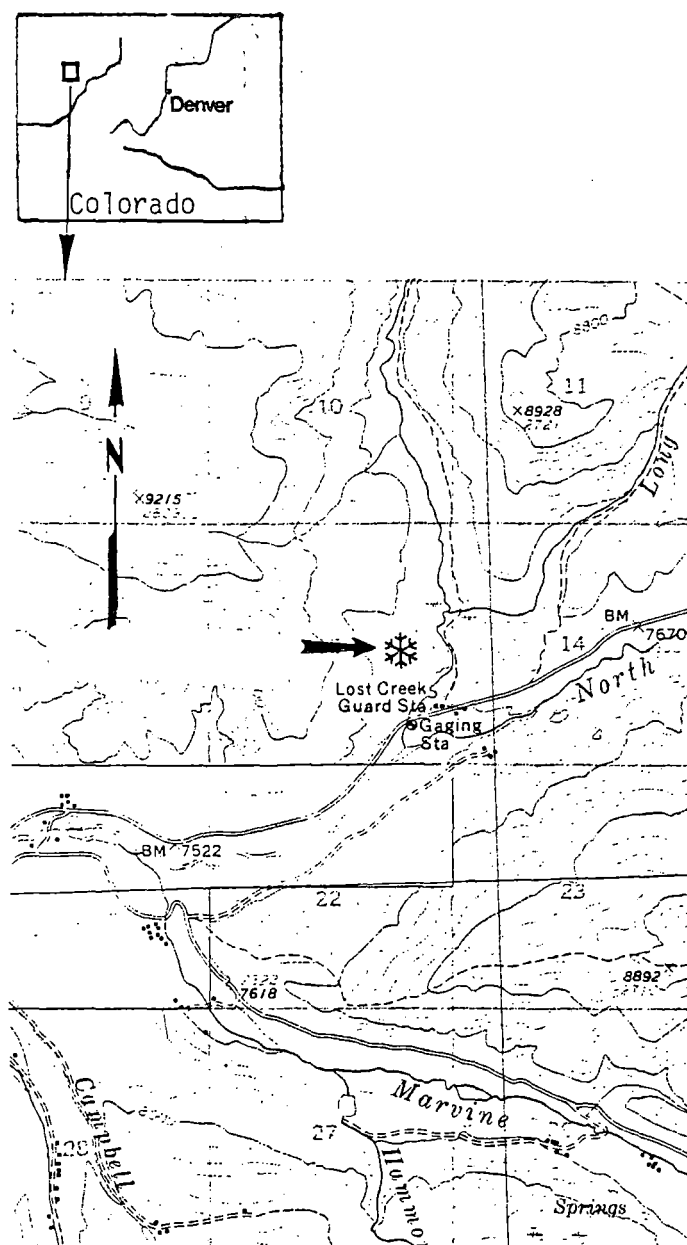


Figure 7. Snow sampling site at Flat Tops Wilderness Area, Colorado, 1981-1982.

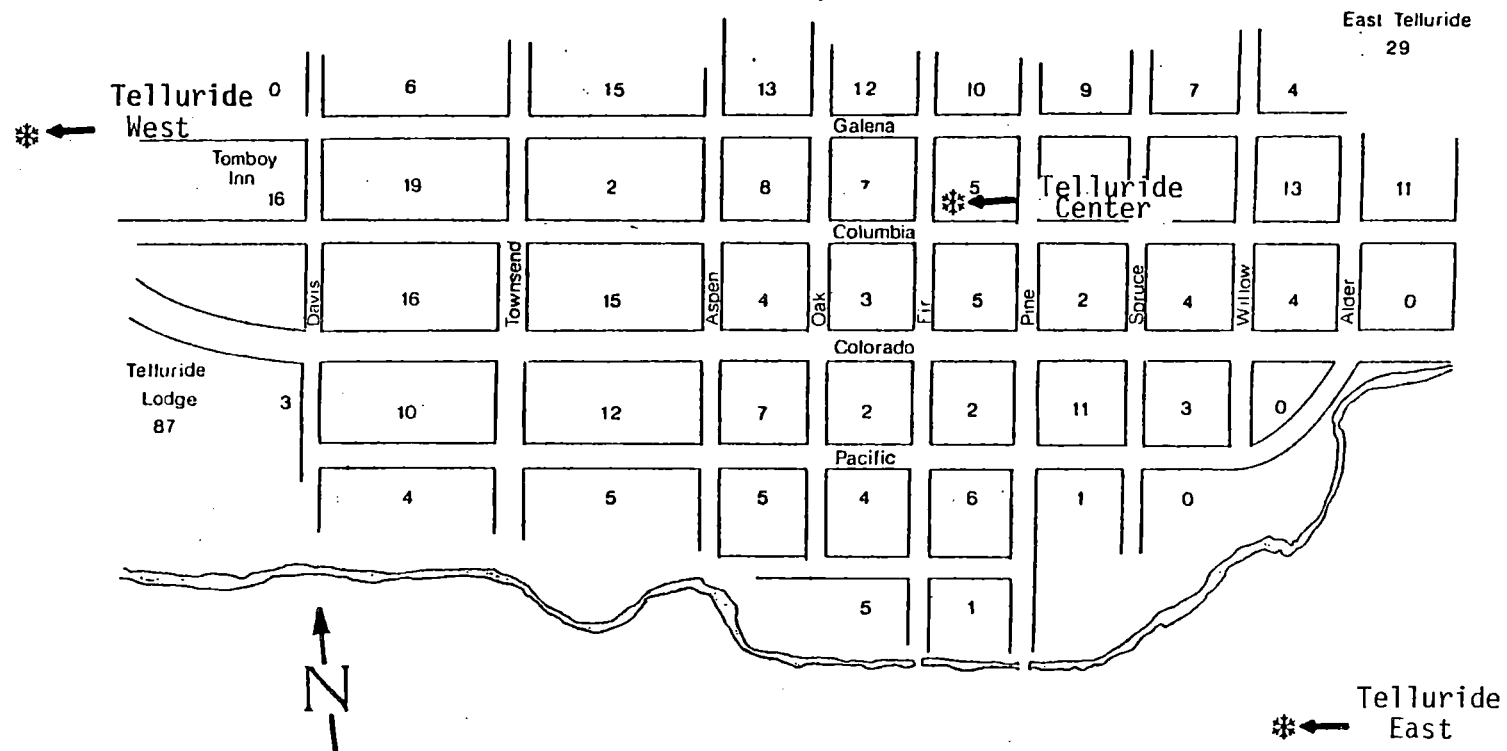


Figure 8. Snow sampling sites at Telluride, Colorado, 1981-1982.
(Groeneveld, 1977)

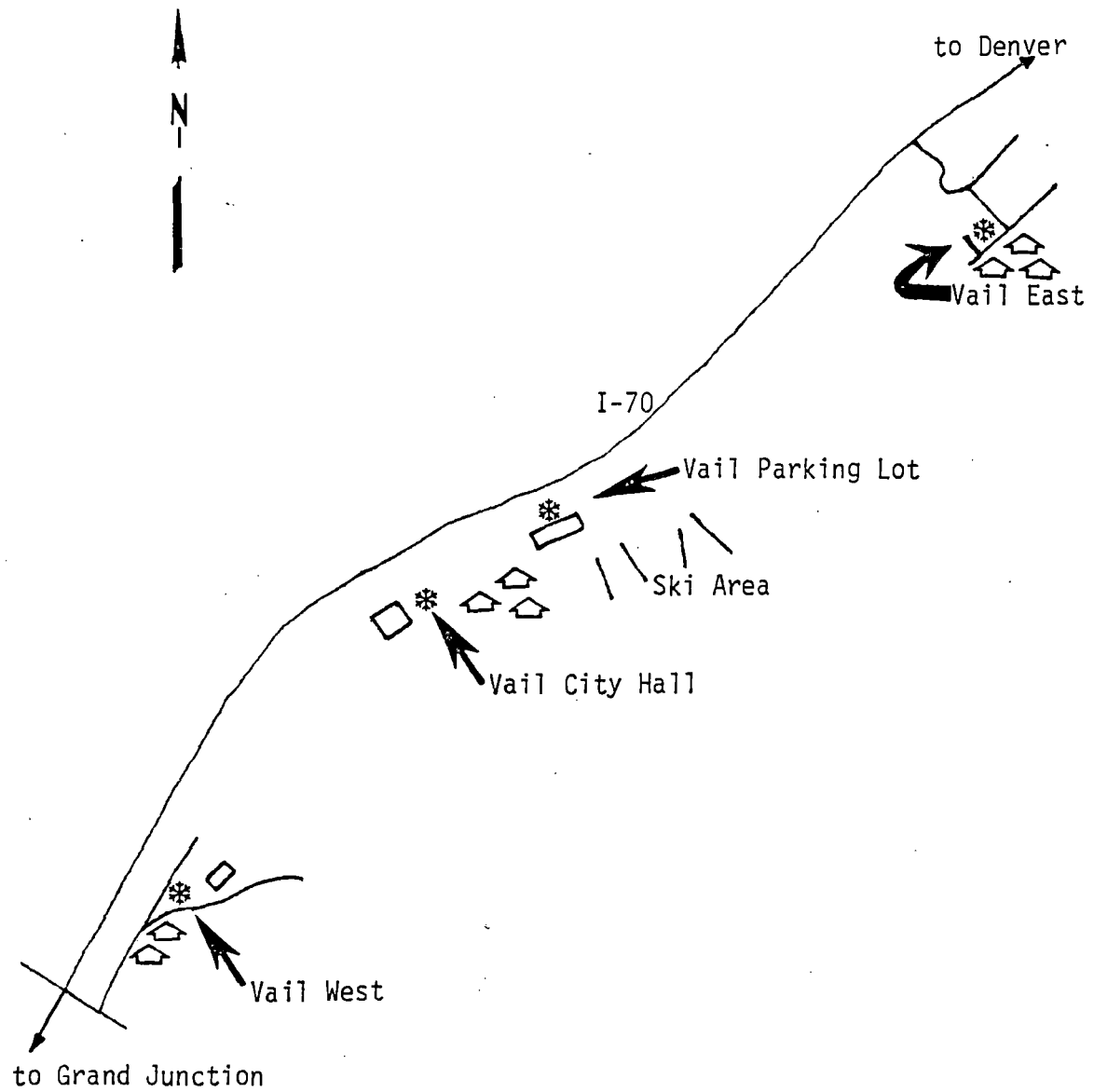


Figure 9. Snow sampling sites at Vail, Colorado, 1981-1982.

The four sampling locations at Vail were less concentrated than those at Telluride. The four locations were: Vail East, Vail Parking Area, Vail City Hall, and Vail West (See Figure 9). All were located in areas that matched the criteria specified for Telluride. The original Vail West site was destroyed by new construction activities and was relocated 40 feet away from its original position and in a safer location. All of the above mentioned sites were located where snow drifting and disturbance were minimized.

Sampling Technique

The following sampling technique was employed at each site:

A four by four foot sheet of clear plastic was placed on the snow surface. It was held in place by four wooden dowels which also served to make the location of each corner. A small amount of snow was placed along the edges of the plastic to hold it in place. The plastic served as a reference point for snow accumulated after the prior sampling period. At the sample collection time, a new sheet of plastic was placed on top of the snowpack next to the previous month's site (See Figure 10).

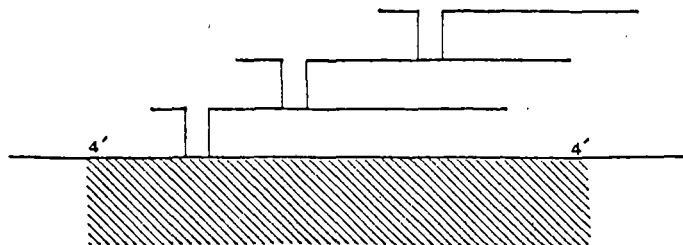


Figure 10. Snow sampling arrangement 1981-1982.

Samples were obtained by digging down to the edge of the plastic and extracting all of the previous month's snowfall using a plastic sampling tube. If inadequate depth prevented the acquisition of a single 500 ml snow-water-equivalent sample, multiple samples were taken and combined. Depth was also recorded prior to preparing a new sampling surface.

Each snow sample was labeled and then melted at room temperature. Upon complete melting pH was measured using a Univar Model 49 digital pH meter. The sample was then frozen, awaiting pickup by the research team.

Laboratory Analysis

All frozen samples were returned to Colorado State University (CSU) and analyzed by the water quality laboratory in the Department of Chemistry. Ion chromatography was used to determine $\text{SO}_4^{=}$ and NO_3^{-} in mg/L.

CHAPTER III

RESULTS AND RELATIONSHIPS

This Chapter discusses relationships (or the lack of) between snow water quality parameters.

Sulphate, Nitrate, and pH Relationships

Table 1 shows concentrations of $\text{SO}_4^{=}$, NO_3^- , and pH for all samples collected from the winter of 1981 and 1982. The snow depth is included and was measured at the time of collection. F^- and Cl^- concentrations were also included in the analysis. F^- proved to be available in very small concentrations and was considered to be inconsequential. Cl^- concentrations generally followed those of $\text{SO}_4^{=}$, and led to the hypothesis that perhaps Ca^{++} was also present. Ca^{++} concentrations were investigated later and are reported further on in the paper. Of primary importance is the pH of snow at each site. Figures 11, 12, and 13 show pH versus time as measured at the Vail, Telluride, and Flat Tops sites. Vail's sites do not correlate with one another and show no obvious pattern. Telluride's three sites track each other very well and show clearly increasing and decreasing trends. Flat Tops' single site remains stable over time. This may mean that Vail's four sites were affected by different pollution sources or mechanisms. The Telluride valley, on the other hand, appears to have been influenced by a relatively homogeneous pollutant situation. If the primary source of pollution is generated locally

Table 1. Analysis of Vail, Telluride, and Flat Tops snow samples obtained 1981-1982.

Sample #	Town	Location	Date	Snow Depth (Inches)	pH	F ⁻ (mg/l)	Cl ⁻ (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ⁻ (mg/l)
1	Vail	East	Dec. 5	8	6.1	0.03	<0.02	0.49	0.48
2	"	"	Jan. 9	30	5.3	0.02	<0.02	0.31	0.53
3	"	"	Feb. 13	7	6.4	0.04	0.15	1.35	0.95
4	"	"	Mar. 13	7	6.1	0.05	0.09	0.14	0.23
5	"	City Hall	Jan. 9	25	5.1	0.05	0.26	0.34	0.74
6	"	"	Feb. 13	10	5.1	0.09	0.79	1.04	1.47
7	"	"	Mar. 13	1 (new)	6.3	0.07	0.16	0.06	0.53
8	"	Parking Lot	Dec. 5	1-2	7.1	0.10	1.09	0.22	1.13
9	"	"	Jan. 9	32	6.3	0.04	0.46	0.43	1.00
10	"	"	Jan. *	?	10.5	0.73	6.43	1.12	15.30
11	"	"	Feb. 13	8	5.2	0.16	2.19	1.51	2.71
12	"	"	Mar. 13	-	6.0	0.01	0.10	<0.05	0.23
13	"	West	Dec. 5	4	5.7	0.38	1.32	0.41	0.63
14	"	"	Jan. 9	30	6.1	0.01	0.17	0.33	0.48
15	"	"	Feb. 13	8	6.1	0.02	0.60	1.16	1.30
16	"	"	Mar. 13	2	4.9	<0.005	0.15	<0.05	0.38
17	Telluride	East	Dec. 2	9	5.4	"	0.13	0.22	0.40
18	"	"	Jan. 7	19.5	5.1	"	0.14	0.28	0.51
19	"	"	Feb. 3	10	6.8	"	0.65	0.49	0.98
20	"	"	Mar. 8	9	5.8	"	0.24	0.22	0.27
21	"	"	Apr. 2	5.5	7.4	"	0.37	0.31	0.55
22	"	West	Dec. 2	7	5.4	"	0.15	<0.05	<0.15
23	"	"	Jan. 7	13	4.6	0.37	0.15	0.31	0.46
24	"	"	Feb. 3	11	6.7	0.16	0.77	0.74	3.09
25	"	"	Mar. 8	3	4.9	0.04	0.18	0.21	0.29
26	"	"	Apr. 2	1.5	7.5	0.06	<0.02	0.24	0.37
27	"	Center	Dec. 2	7	5.4	0.03	"	0.30	0.33
28	"	"	Jan. 7	23	4.4	0.02	"	0.19	<0.15
29	"	"	Feb. 3	10	7.0	0.01	"	0.37	0.37
30	"	"	Mar. 8	7.5	5.5	0.01	"	0.13	0.41
31	"	"	Apr. 2	3.5	7.5	0.01	0.10	0.15	0.25
32	Flat Tops	"	Dec. 11	?	5.2	<0.005	<0.02	0.37	0.25
33	"	"	Jan. 10	?	5.0	"	"	0.30	0.31
34	"	"	Feb. 12	?	5.0	"	"	0.48	0.28
35	"	"	Mar. 14	?	5.2	"	"	<0.05	<0.15

*contaminated by street salts.

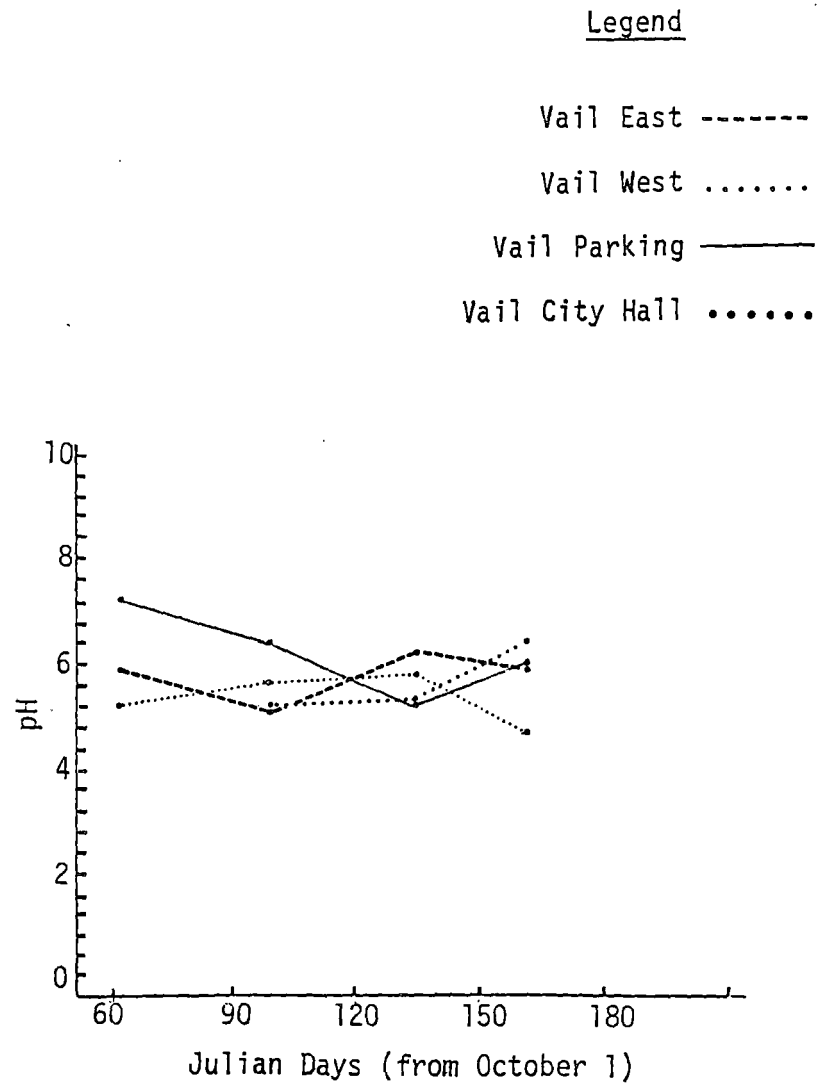


Figure 11. pH vs. Julian Days, Vail, Colorado, water year 1981-1982.

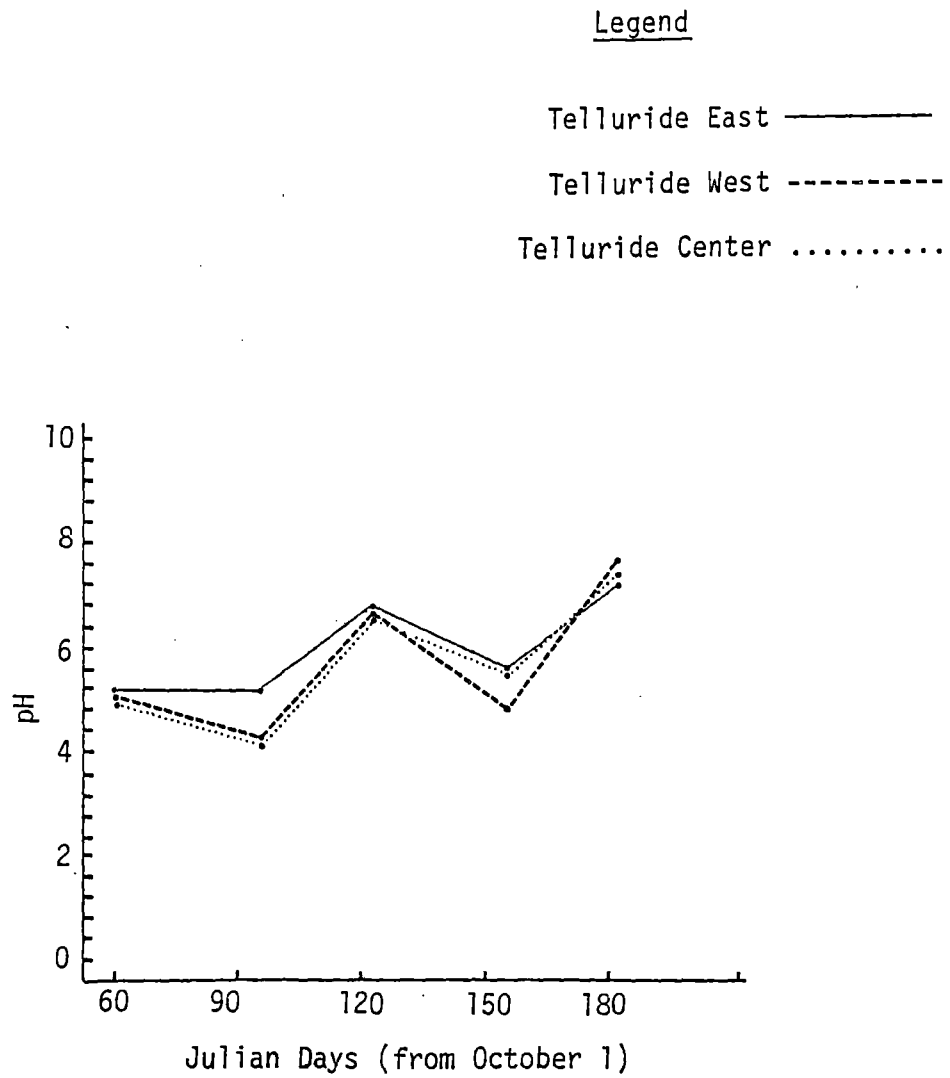


Figure 12. pH vs. Julian Days, Telluride, Colorado, water year 1981-1982.

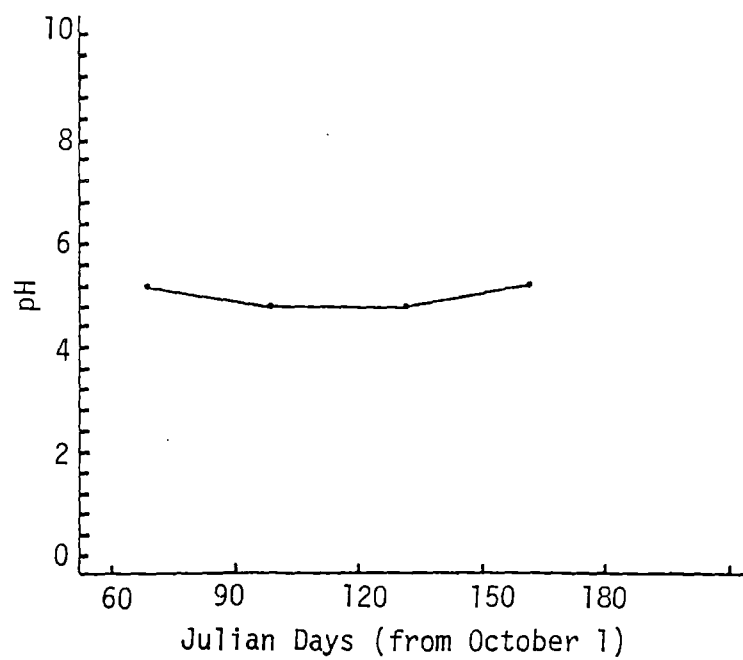


Figure 13. pH vs. Julian Days, Flat Tops Wilderness Site, Colorado, water year 1981-1982.

in Vail, then the local dispersion patterns would be responsible for variations of pH. Wind patterns at Vail were noticeably more erratic than at Telluride, and wind speeds were generally greater. Concentrations of snowpack pollutants and pH were, therefore, difficult to correlate to atmospheric pollution at Vail:

Flat Tops pH measurements indicate stability and perhaps a lower than expected pH value. Since no contamination was local in Flat Tops precipitation, it can be assumed that the acidity within the snowpack is from regional and/or global sources not yet identified. Plots of $\text{SO}_4^{=}$ and NO_3^{-} versus time at Vail and Telluride (Figures 14, 15, 16, and 17) show distinctly increasing and decreasing trends attributed to the dispersion mechanisms unique to each site. These same trends were not found at Vail when examining pH versus time, possibly indicating that $\text{SO}_4^{=}$ and NO_3^{-} were not the only constituents controlling pH at that site.

A correlation between $\text{SO}_4^{=}$ and pH or NO_3^{-} and pH was looked for to explain the presence of abnormally low pH values (less than 5.6) within the snowpack. Figures 18 to 22 show that no such correlation was found at Vail, Telluride, and Flat Tops. This would seem to contradict the theory that most acidity in precipitation can be attributed to $\text{SO}_4^{=}$ and NO_3^{-} . Previous investigations have shown that 60 to 70 percent of the potentially available hydrogen ions in precipitation originate from SO_2 , and to some extent from H_2S , which has been oxidized to H_2SO_4 (Bolin and Granat, 1973). NO_x , which has been oxidized to HNO_3^{-} , then follows in importance. The acidity of precipitation also depends on the contribution of alkaline ions (e.g., Ca^{++}) which neutralize the acids (Forland and Gjessing, 1975).

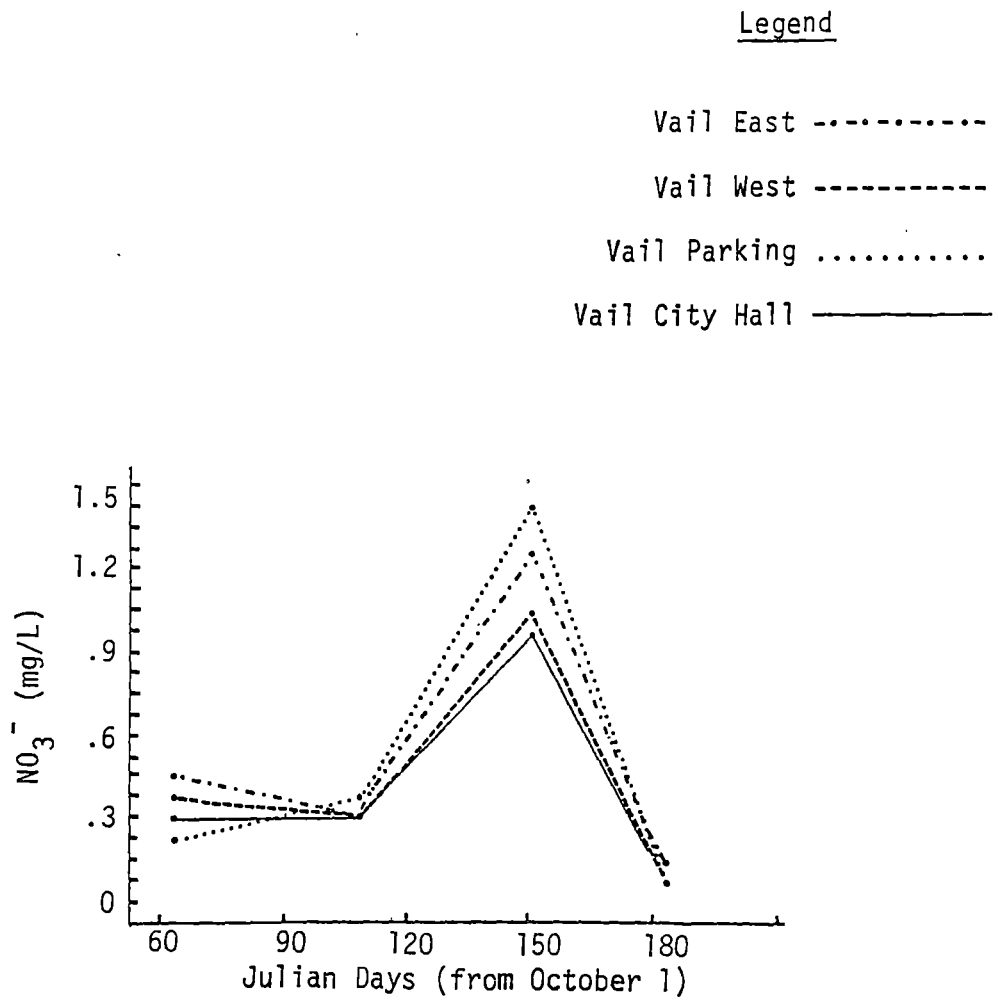


Figure 14. NO_3^- vs. Julian Days, Vail, Colorado, water year 1981-1982.

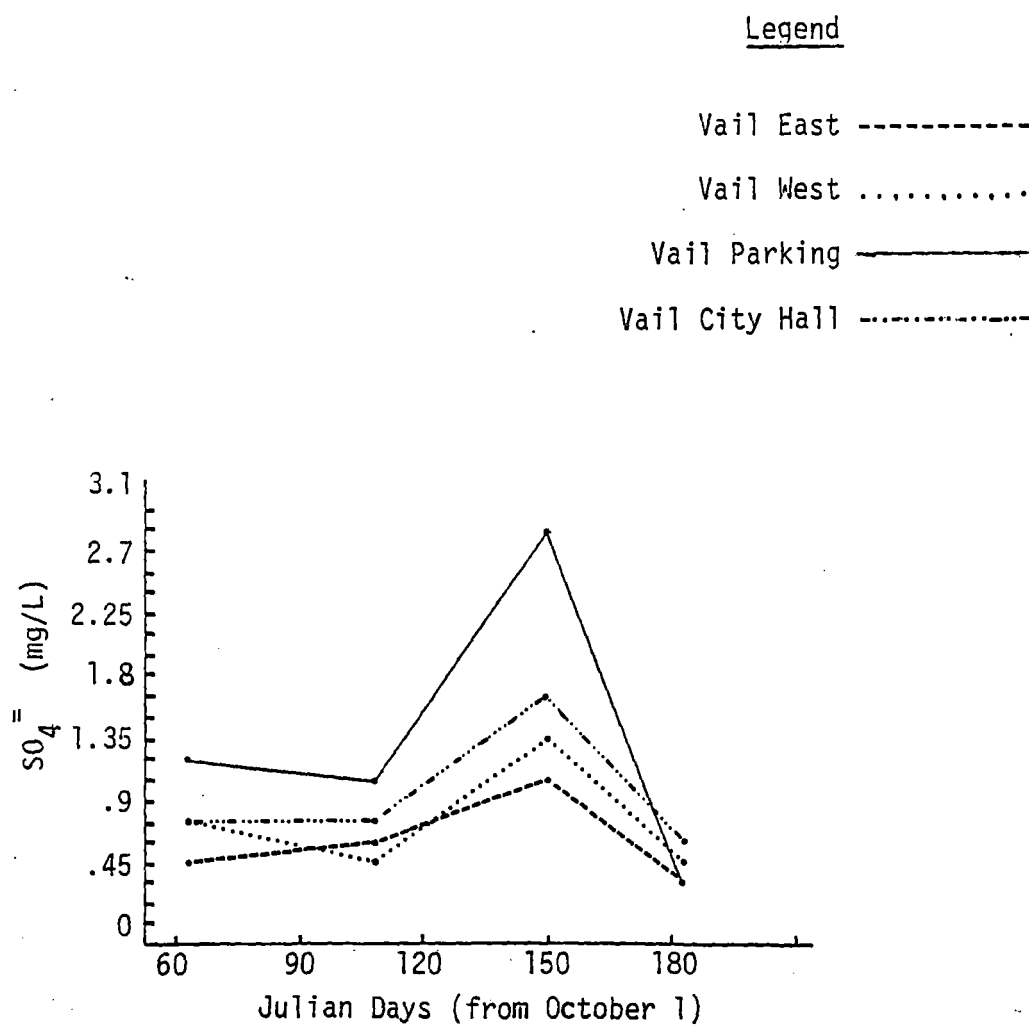


Figure 15. $\text{SO}_4^{=}$ vs. Julian Days, Vail, Colorado, water year 1981-1982.

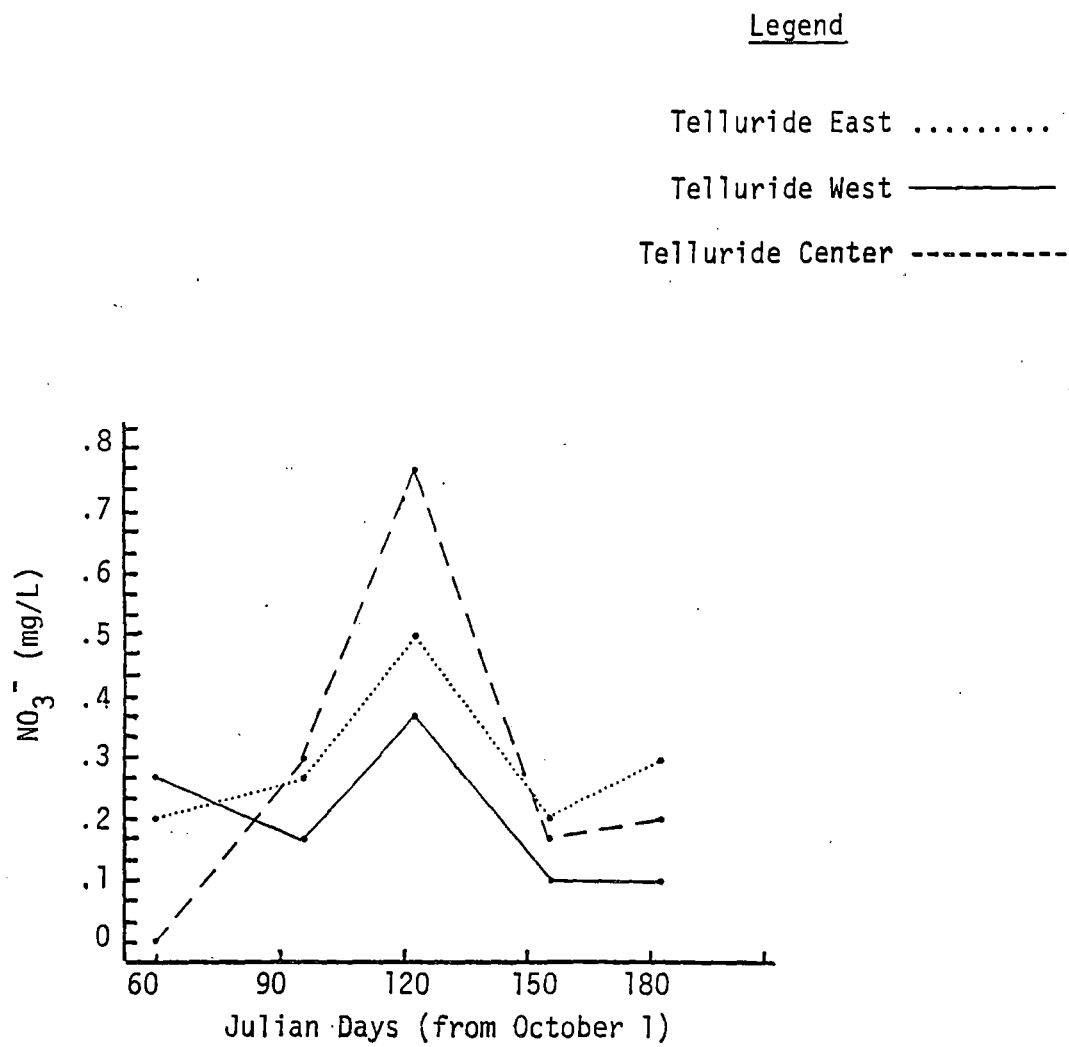


Figure 16. NO_3^- vs. Julian Days, Telluride, Colorado, water year 1981-1982.

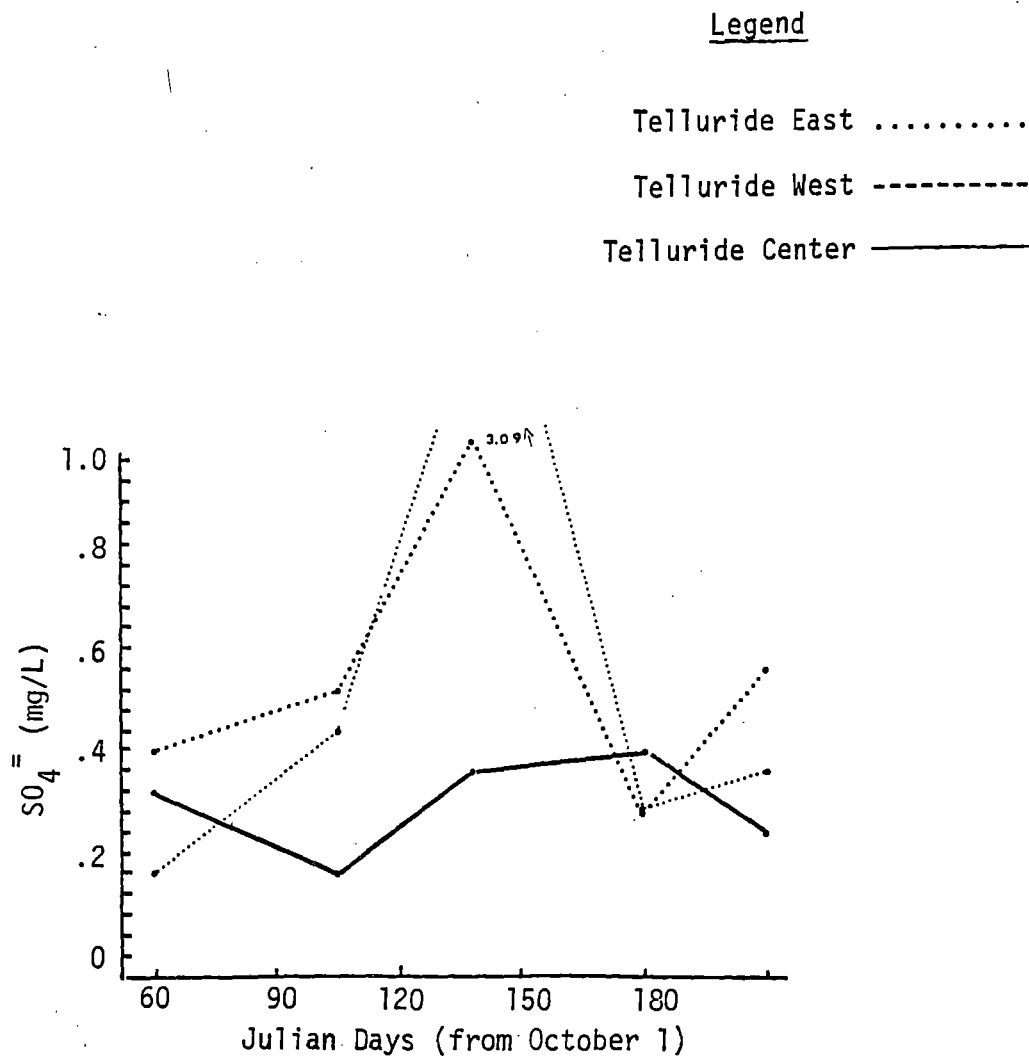


Figure 17. $SO_4^{=}$ vs. Julian Days, Telluride, Colorado, water year 1981-1982.

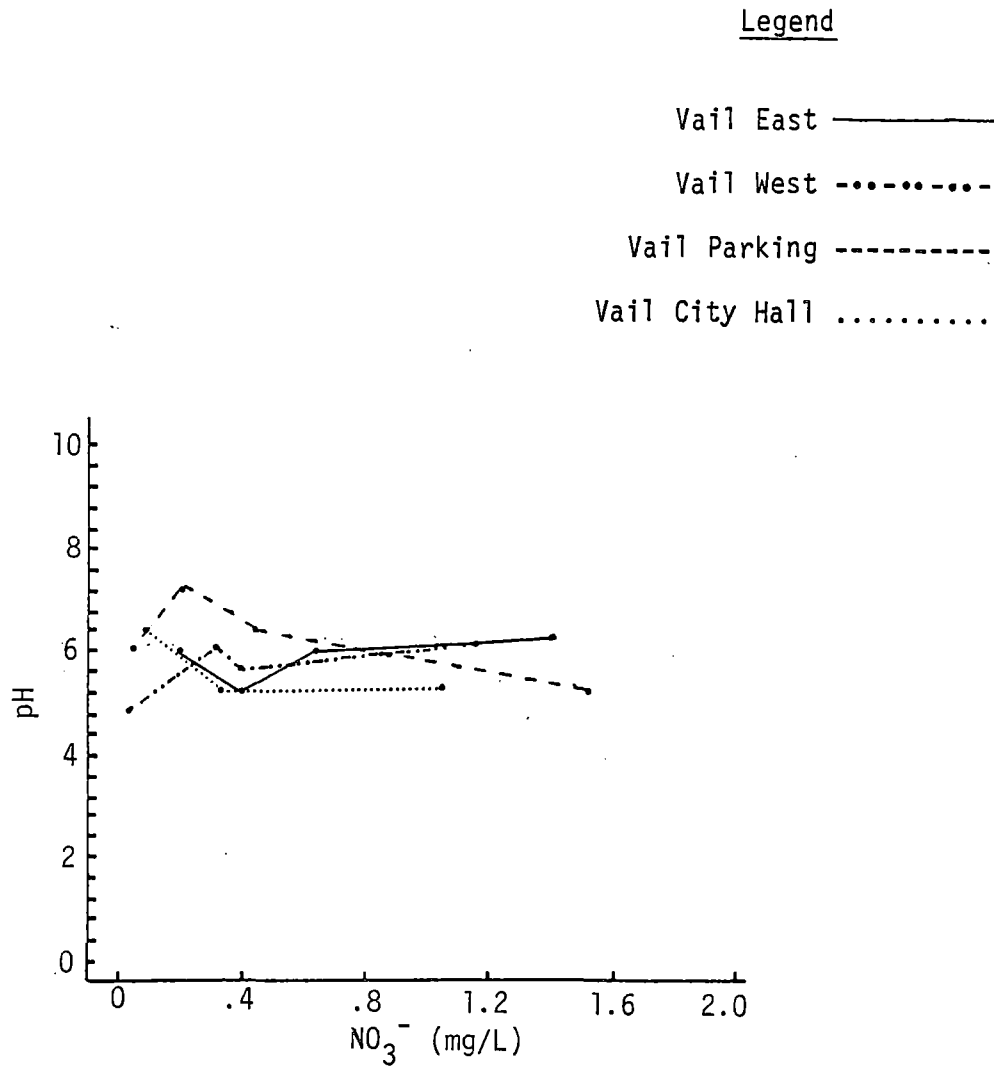


Figure 18. pH vs. NO_3^- , Vail, Colorado,
1981-1982.

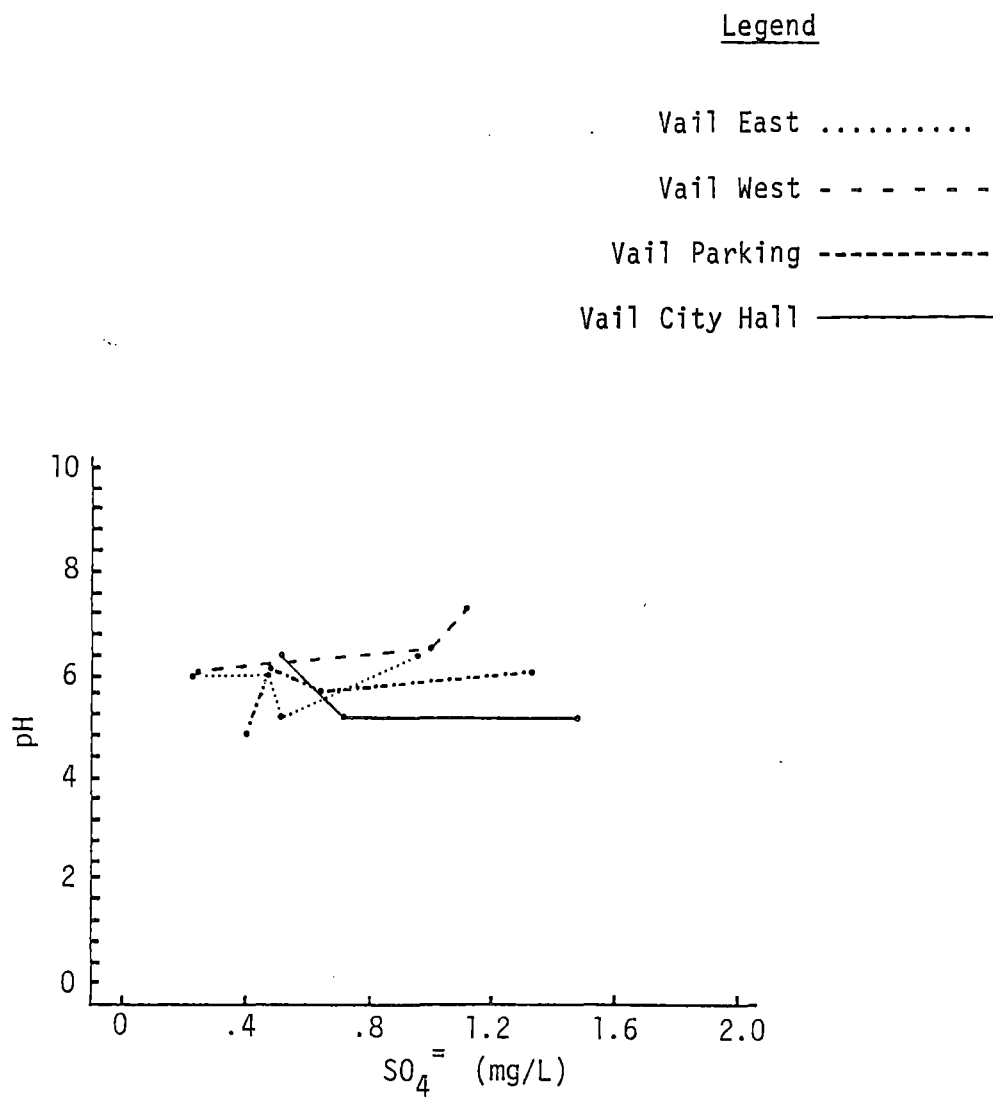


Figure 19. pH vs. SO_4^{2-} , Vail, Colorado,
1981-1982.

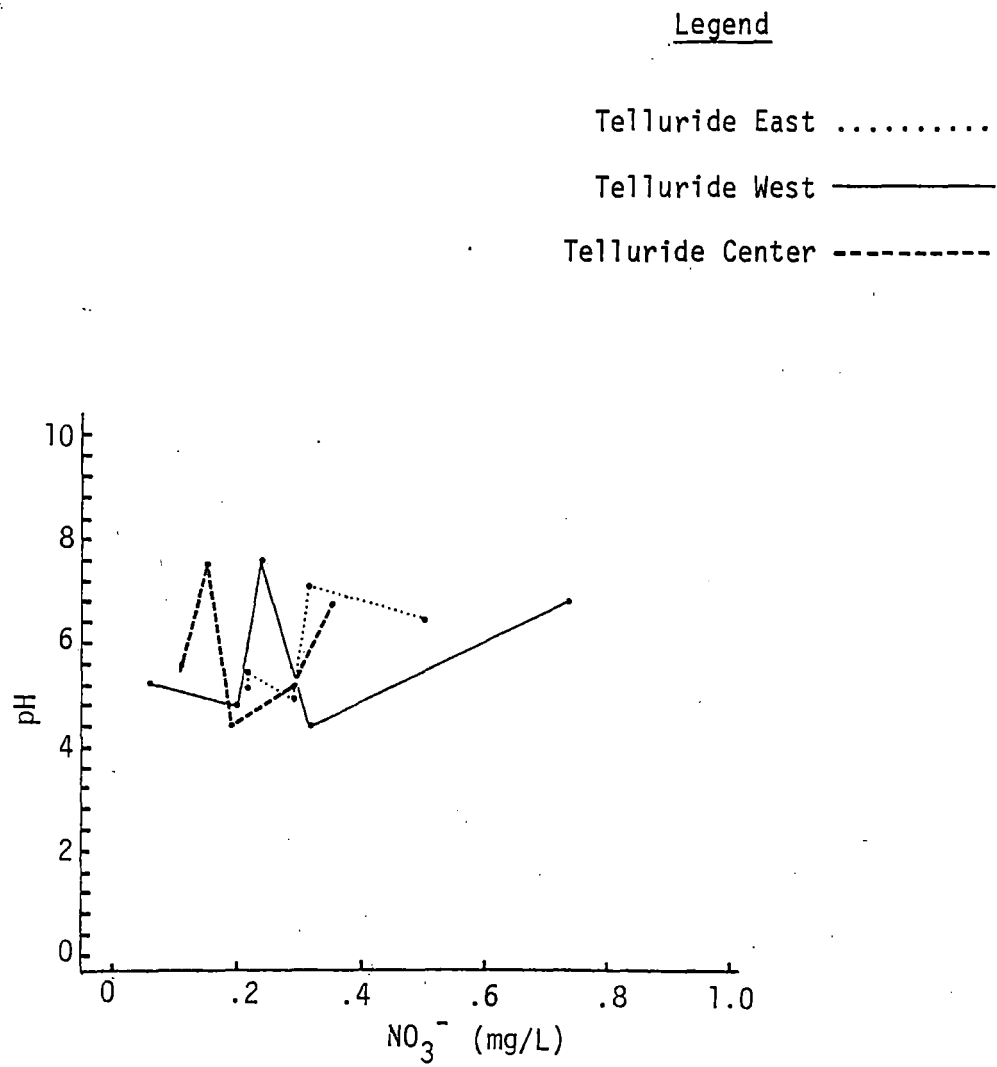


Figure 20. pH vs. NO_3^- , Telluride, Colorado,
1981-1982.

Legend

Telluride East

Telluride West -----

Telluride Center ———

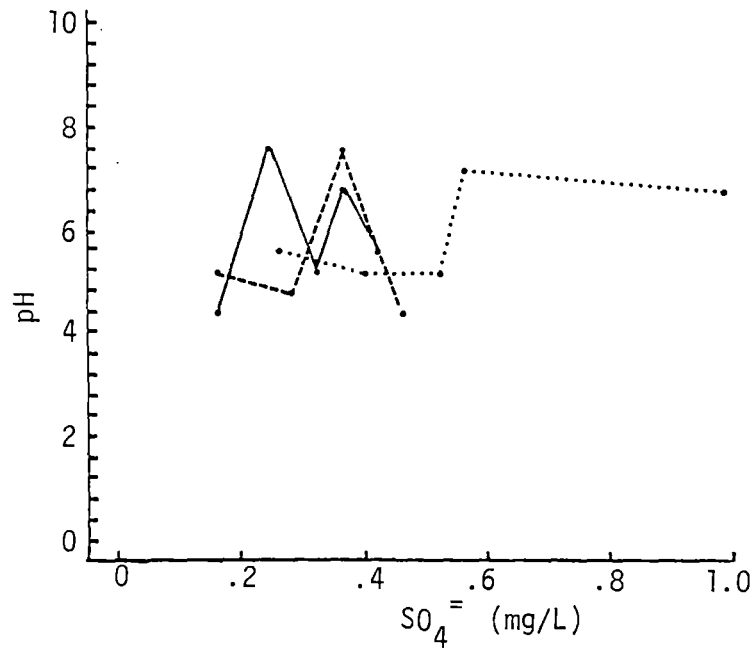


Figure 21. pH vs. $\text{SO}_4^{=}$, Telluride, Colorado,
1981-1982.

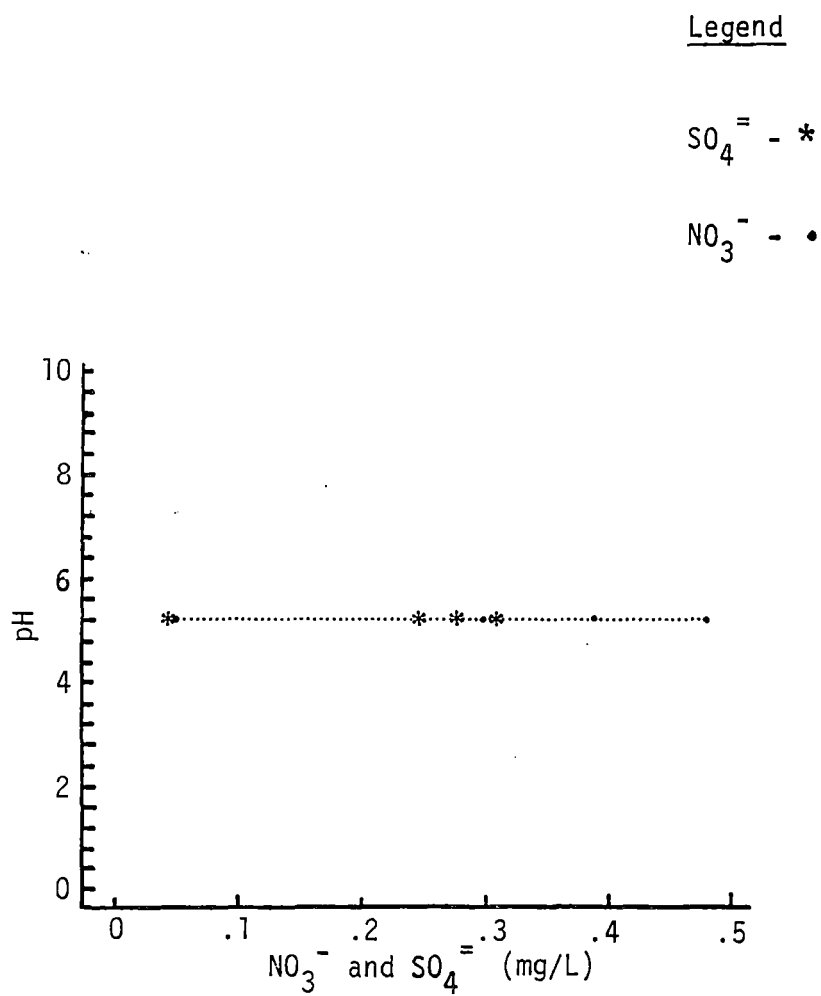


Figure 22. pH vs. NO_3^{-} and $\text{SO}_4^{=}$, Flat Tops Wilderness, Colorado, 1981-1982.

Influence of Calcium on pH

Figures 18 to 22 show no evidence of a relationship between pH and the concentration of NO_3^- or $\text{SO}_4^{=}$ at Vail, Telluride, or Flat Tops. Other constituents must therefore be influencing pH. The snow analysis reported in Table 1 showed significant concentrations of Cl^- in the Vail and Telluride samples. This led to the hypothesis that Ca^{++} (as CaCl_2) might be influencing snow pH in these areas.

A close examination of our samples revealed calcium in concentrations from 0.18 mg/L to 12.56 mg/L. The highest calcium concentrations were recorded at the Vail parking lot site and may have been contaminated by CaCl_2 . The other Vail and Telluride sites were not exposed to direct contamination by street salts yet concentrations of Ca^{++} up to 9.14 mg/L were recorded. The source of Ca^{++} within our samples has yet to be positively identified. It may be from:

- 1.) Wind deposited calcium of natural (rock or soil) or anthropogenic (street salts) origin.
- 2.) Fly ash coming from local combustion of wood and coal.
- 3.) Fly ash coming from regional or continental combustion of coal.

The Flat Tops samples had very low Ca^{++} concentrations of .22 mg/L (sample 32) and .35 mg/L (sample 33). Their $\text{SO}_4^{=}$ and NO_3^- concentrations were nearly the same, possibly indicating a background level of contamination from regional or continental sources.

A preliminary investigation of the relationship between the neutralizing capacity of calcium and the acidity associated with $\text{SO}_4^{=}$ and NO_3^- showed calcium to be the primary control of pH on snow samples which have been contaminated. Figure 23 shows an exponential

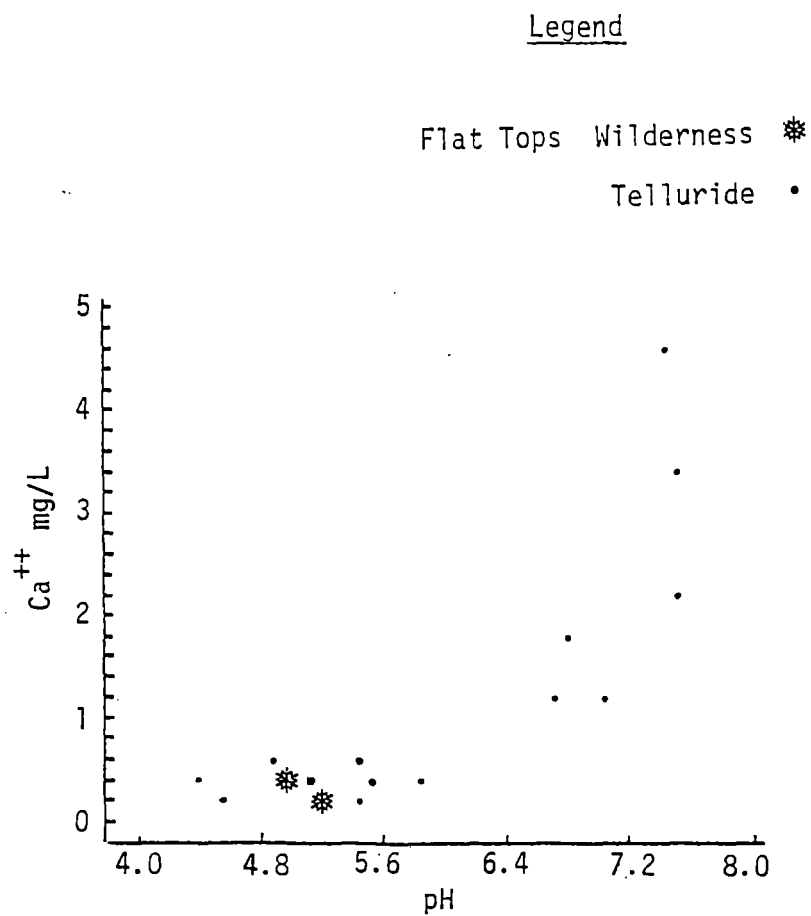


Figure 23. Ca^{++} mg/L vs. pH, Telluride and Flat Tops Wilderness, Colorado, 1981-1982.

relationship between the concentration in mg/L of calcium from 16 Telluride and Flat Tops samples and pH.

If a plentiful supply of calcium exists within the snowpack and is not accompanied by a corresponding increase in ions such as $\text{SO}_4^{=}$ or NO_3^{-} , the expected pH will be greater than 5.6 to 5.8. A further investigation of calcium and its role with pH led to the assumption that calcium does indeed control pH even if similar concentrations of $\text{SO}_4^{=}$ and NO_3^{-} are present. Figure 24 shows a plot of calcium concentrations in mg/L versus pH using values from Telluride, Colorado, 1980-1981; Flat Tops Wilderness Area, Colorado, 1981-1982; Cameron Pass, Colorado, 1982; and Keystone, Colorado, 1983.

A good correlation can be seen; this indicates the importance of calcium as a control of pH in snow. This relationship may not hold true as stronger acids enter the snowpack as is the case in parts of Scandinavia.

Calcium is a common element in nature, particularly in arid lands, and used as CaCl_2 to improve traction on roads. It is also a by-product of the combustion of some coal. Ash may contain 3% CaO which may be released through the combustion of residential fuels (Newman, 1975).

Measurements of pH

The question of what the pH of snow is when it falls, and what the areal variability of pH is within the watershed remained to be answered. On October 31, 1982, a snow sampling trip was undertaken to:

- 1.) Measure the pH of freshly fallen snow.
- 2.) Determine the variability of pH within a watershed.

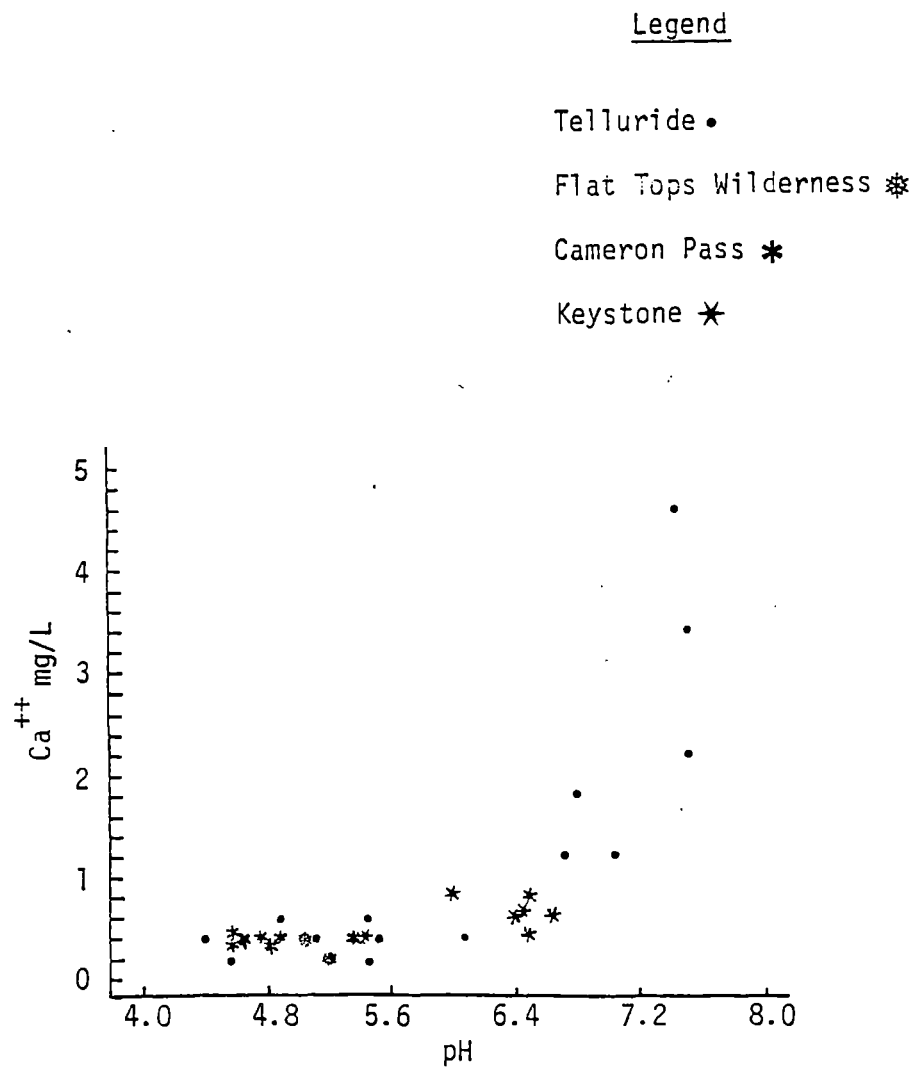


Figure 24. Ca⁺⁺ mg/L vs. pH from Telluride, Colorado, 1981-1982; Flat Tops Wilderness, Colorado, 1981-1982; Cameron Pass, Colorado, 1982; and Keystone, Colorado, 1983.

3.) Determine the best sampling and storage techniques for snow measurements.

On the day of the trip a major winter storm event occurred in the Colorado Rockies. The research team drove to Cameron Pass 70 miles west of Fort Collins (See Figure 1) and selected the American Lakes Drainage as a watershed to monitor (See Figures 25, 26, and 27). A total of 10 sites were selected at approximately 600 m intervals extending 4 Km up into the Drainage and gaining 300 m in elevation. This sampling arrangement allowed a uniform set of samples to be obtained throughout the length of the watershed. The area is partially isolated from traffic (some snowmobiles, though) with no industry or grazing. Access in winter is by skiing or snow machine via the Michigan Ditch. Twenty sample bottles, 2 liters in size, were washed with distilled water prior to leaving and were used to obtain all samples. The snow was no older than six hours and all samples were obtained well off the principal trail. Duplicates were taken at each site. As soon as sampling was completed, the containers were returned to the laboratory and stored at 4°C. On November 2, 1982, the samples were removed from refrigeration and, still partially frozen, were allowed to melt out at room temperature. The pH of each sample was then measured using an Extech 651 pH/mV meter with temperature correction and calibrated to buffer solutions of 4.0, 6.0, 7.0, and 10.0 pH. Table 2 shows pH measurements obtained on November 2, 1982.

Three of the samples (3a, 9a, 10b) were very unstable when the probe was inserted into the solution. Each of the three reacted in the same manner by displaying a steadily rising pH value well beyond naturally occurring pH's. Despite considerable time and care in

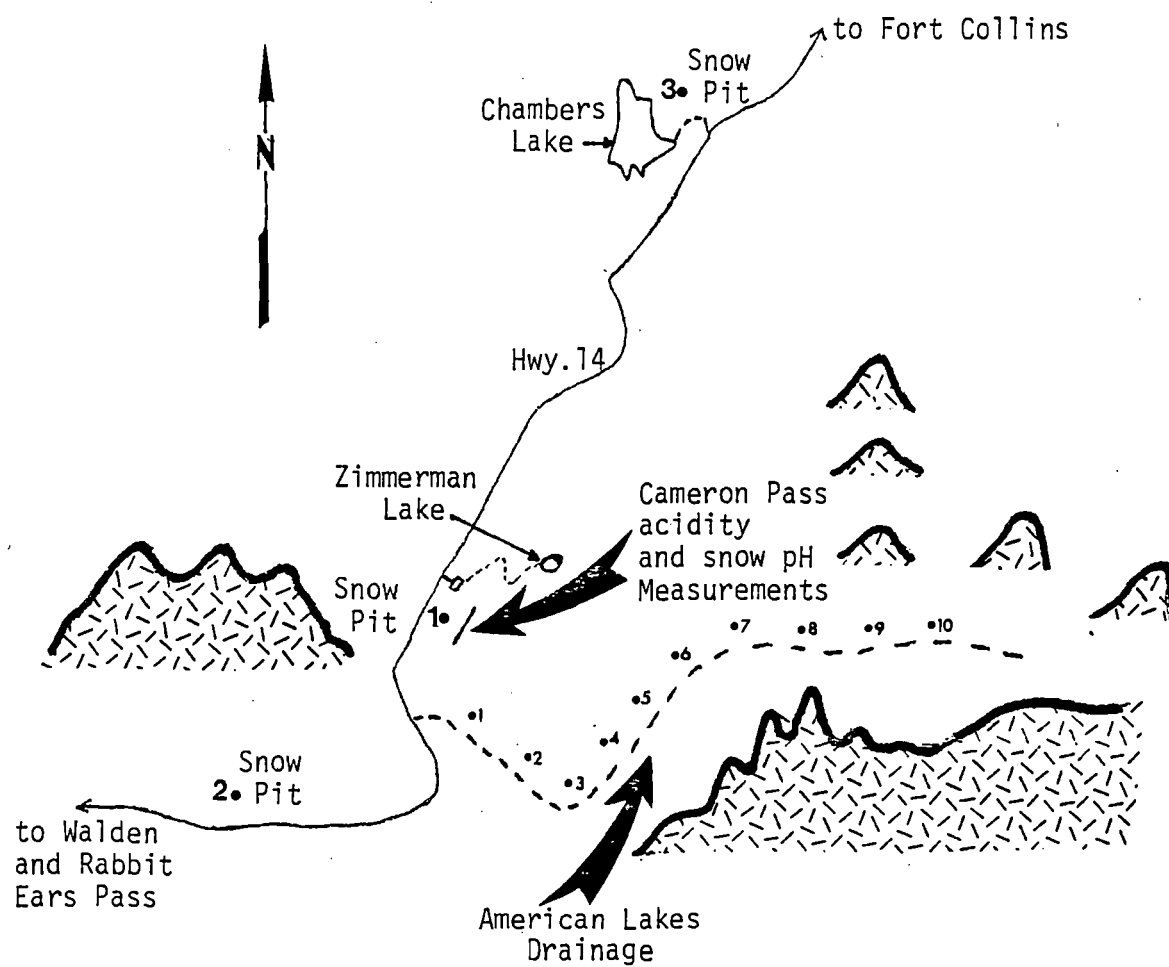


Figure 25. Snow sampling sites at Cameron Pass, Colorado, 1982-1983.

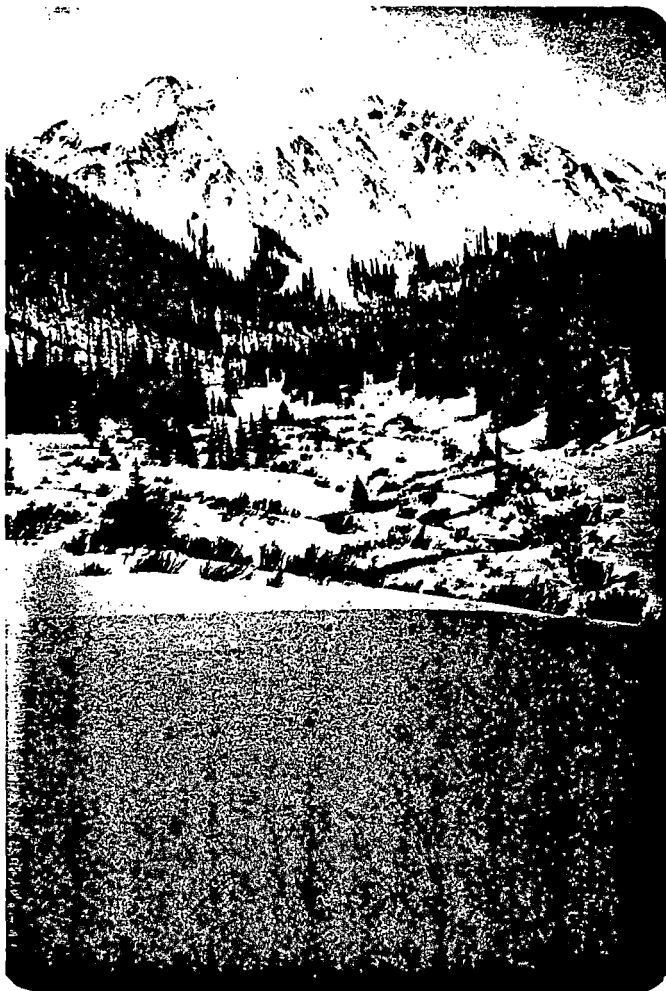


Figure 26. American Lakes Drainage, Colorado.



Figure 27. Sampling snow in American Lakes Drainage, Colorado, 1982.
Note the use of plastic laboratory gloves to prevent wool fiber or perspiration contamination.

cleaning and rinsing sample containers it may be that these three were subject to contamination, perhaps by soap or a resistant material from a previous experiment. The slightest concentration of such a contaminant could drastically affect pH, therefore, these three samples have been excluded from further analysis. New containers were used for subsequent work.

Table 2. pH measurements of snow from American Lakes Drainage, Colorado, obtained 10-31-82 and measured in the laboratory, 11-2-82.

Sample Number	pH	Sample Number	pH
1a	4.80	6a	4.62
1b	*	6b	4.68
2a	*	7a	4.59
2b	4.60	7b	4.60
3a	4.58	8a	*
3b	4.76	8b	4.66
4a	4.58	9a	4.50
4b	4.71	9b	4.66
5a	4.53	10a	4.56
5b	4.56	10b	4.65

mean: 4.63

standard deviation: 0.07

range: 4.50-4.80

*samples removed due to possible contamination.

The 17 remaining values have a geometric mean of 4.63, a standard deviation of 0.07, and a range of pH of 4.50 to 4.80. The values are remarkably close to each other and may indicate:

- 1.) The pH of freshly fallen snow varies little within an uncontaminated watershed.
- 2.) Natural pH variability in snow, sampling methods, and laboratory technique produce measurements within 0.2 pH unit.

If the statements listed above are valid, then more questions need to be answered. One important question was how long will our samples retain their pH value, and what is the proper storage technique?

In order to answer this question, we transferred our samples to clean 150 ml containers and filled them completely. We then stored them at 4°C overnight and once again ran pH. This was completed on November 5, 1982. The pH was measured again on November 29, 1982, and January 6, 1983. Table 3 summarizes our results. The mean pH of 4.63 on the initial run rose to 4.69, 4.84, and 4.97 by January 6, seven weeks after sampling.

The four days of pH measurements indicated how important it is to perform pH measurements of snow either in the field or shortly after returning to the laboratory. Storage of snowmelt water in containers with little or no air seemed to be helpful in preserving the original pH value. Agitation of samples was avoided, and the most accurate measurements of pH were made within three days of sampling. It was discovered that a volume of 500 ml meltwater was necessary to perform the desired tests in our laboratory. Duplicate samples proved to be valuable and will be used in future work.

Table 3. pH measurements of snow from American Lakes Drainage, Colorado, obtained 10-31-82 and measured in laboratory 11-3-82, 11-5-82, and 1-6-83.

<u>11-3-82</u>			
Sample Number	pH	Sample Number	pH
1a	4.83	6a	4.77
1b	*	6b	4.71
2a	*	7a	4.66
2b	4.70	7b	4.66
3a	4.61	8a	*
3b	4.79	8b	4.66
4a	4.78	9a	4.56
4b	4.68	9b	4.70
5a	4.57	10a	4.63
5b	4.61	10b	4.71

mean: 4.68

standard deviation: 0.07

range: 4.57-4.83

*samples removed due to possible contamination

<u>11-5-82</u>			
Sample Number	pH	Sample Number	pH
1a	4.90	6a	4.98
1b	*	6b	4.76
2a	*	7a	4.82
2b	4.89	7b	5.09
3a	4.86	8a	*
3b	4.75	8b	4.78
4a	4.69	9a	4.45

Table 3. (cont'd)

Sample Number	pH	Sample Number	pH
4b	4.66	9b	4.72
5a	4.69	10a	4.82
5b	4.66	10b	5.22

mean: 4.76

standard deviation: 0.15

range: 4.45-5.22

*samples removed due to possible contamination.

<u>1-6-83</u>			
Sample Number	pH	Sample Number	pH
1a	4.91	6a	5.20
1b	*	6b	5.07
2a	*	7a	4.60
2b	4.82	7b	5.55
3a	4.60	8a	*
3b	4.77	8b	4.90
4a	4.63	9a	4.55
4b	4.82	9b	4.77
5a	4.50	10a	4.95
5b	4.63	10b	5.34

mean: 4.78

standard deviation: 0.18

range: 4.50-5.55

*samples removed due to possible contamination.

These conclusions may seem obvious, yet little was known about the relative purity of snow in the western United States and how very sensitive pH is when measured in an unbuffered solution. The utmost care must be utilized when determining pH in such solutions and a back-up measurement, using laboratory grade pH paper strips, may be desirable.

In order to check the validity of the previous experiment and to determine whether or not pH measurements will change with altitude (American Lakes is at an elevation of 9000 feet, our laboratory is at 5000 feet), a second group of 4 samples were independently analyzed to see if the same results would occur. These 4 samples were obtained near the summit of Cameron Pass. The pH was measured in the field on October 31, 1982, and in the laboratory on November 1, 1982, November 3, 1982, November 4, 1982, November 5, 1982, and January 6, 1983. Table 4 summarizes our results.

Table 4. pH measurements of snow from Cameron Pass, Colorado, obtained 10-31-82 and measured on 10-31-82, 11-1-82, 11-4-82, 11-5-82, and 1-6-83.

Sample No.	pH 10-31-82 (at site)	pH 11-1-82	pH 11-3-82	pH 11-4-82	pH 11-5-82	pH 1-6-83
1	4.92	5.08	5.63	5.73	5.74	5.93
2	4.80	4.95	5.60	5.25	5.80	5.98
3	4.68	4.58	4.56	4.67	4.62	4.70
4	4.50	4.63	4.71	5.05	5.06	4.98

Notice that samples 1, 2, and 4 show a clearly increasing pH over time, with samples 1 and 2 reaching a higher endpoint (pH 5.93 and pH 5.98) than sample 4 (pH 4.98). Sample 3 remains relatively unchanged over time. All were obtained at the same site at the same time. They were stored and measured in the same manner. Why the pH of three of the four samples has risen while the fourth hasn't remains to be investigated. The experiment did confirm our original hypothesis of an increasing pH over time occurring with most samples. Note too that the pH measured on October 31, 1982, differs little from that measured on November 1, 1982, representing minor effects of altitude change on pH, if any. What increase in pH that occurred was likely due to pH increase over time as noted above.

The question of whether or not freezing and/or refrigeration affects pH was of interest to the project, and also what effect the freeze-thaw cycle has on progressive pH measurements. An experiment was designed to answer these questions by using 4 snow samples from October 31, 1982 (still frozen), and 3 distilled water samples (See Table 5). They were:

1-7-82 - Sample 1 - Snow - original pH 5.30, pH at beginning of experiment 5.80.

Sample 2 - Snow - original pH 5.30, pH at beginning of experiment 5.80.

Sample 3 - Snow - original pH 5.30; pH at beginning of experiment 5.81.

Sample 4 - Snow - original pH 5.30; pH at beginning of experiment 5.88.

Sample 5 - Distilled H₂O - pH at beginning of experiment 6.18.

Sample 6 - Distilled H₂O - pH at beginning of experiment 6.18.

Sample 7 - Distilled H₂O - pH at beginning of experiment 6.19.

Samples 1 and 2 were frozen and then thawed. Sample 3 was refrigerated, and sample 4 was left at room temperature. Sample 5 was frozen, sample 6 was refrigerated, and sample 7 was left at room temperature. Table 5 shows the results after two cycles covering five days.

Table 5. pH measurements of snow obtained from Cameron Pass, Colorado, on October 31, 1982 (frozen while in storage), and distilled water using different storage methods.

Sample No.	Source	pH 1-7-83	Storage Method	pH 1-12-83
1	snow	5.80*	melted, frozen melted	5.98
2	snow	5.80*	melted, frozen melted	5.91
3	snow	5.81*	melted, refrigerated at 4°C	5.93
4	snow	5.88*	melted, stored at 20°C	6.25
5	distilled water	6.18	frozen, melted	6.29
6	distilled water	6.18	refrigerated at 4°C	6.50
7	distilled water	6.19	stored at 20°C	6.28

*These snow samples had an original pH of 5.30 and had risen to the indicated pH while frozen in storage.

An increase in pH occurred with all samples. Although the increases may have been time-dependent, freezing or refrigerating appears to better preserve samples than leaving at room temperature.

A new set of snow samples were obtained on January 13, 1983, from Keystone, Colorado (See Figure 1), and put through a similar experiment. Samples a and b were each divided into 4 equal volumes of snow and stored in the following manner:

Samples 1a, 1b were melted and pH was measured on January 15, 1983.

Samples 2a, 2b were stored in a freezer until January 17, 1983, when pH was measured.

Samples 3a, 3b were stored in a freezer until January 20, 1983, when pH was measured.

Samples 4a, 4b were stored in a freezer until January 24, 1983, when pH was measured.

The results of these measurements are shown in Table 6.

The pH measurements on both samples a and b tended to increase slightly for the first six days and then decrease after ten days. Best storage technique was therefore determined to be freezing samples immediately and upon arrival at the laboratory conducting measurements as soon as possible. Several sources of error are inherent to any snow sampling program involving pH. The primary cause is due to the lack of both buffering material (e.g., Ca^{++}) and strong acids (e.g., H_2SO_4). Most pH electrodes are accurate to within ± 0.1 pH unit. This is attainable when using buffer solutions, but not always true when melted snow with concentrations of less than 1 mg/L Ca^{++} , NO_3^- , and $\text{SO}_4^{=}$ is measured. In such a pure solution, pH readings may

Table 6. pH of snow obtained on January 13, 1983, from Keystone, Colorado, using varying storage times.

Sample No.	Original pH	Storage time in freezer (days)	pH
1a	6.50	0	6.50
1b	6.00	0	6.00
2a	6.50	3	6.53
2b	6.00	3	6.34
3a	6.50	6	6.67
3b	6.00	6	6.45
4a	6.50	10	6.19
4b	6.00	10	6.08

"drift" causing significant errors, particularly if an arbitrary time limit is used when taking the reading. These errors can be minimized by using an electrode and pH meter calibrated to buffer solutions within the expected range of snow samples and by being exceptionally careful not to contaminate the sample. Contamination may occur from using an apparently clean and washed container yet still having micro-contaminants which will affect the pH measurement. Another source of contamination is organic material which has fallen onto the snowpack and become incorporated into the sample. If this material is not removed in some way, it will react with the snowmelt and change pH and perhaps the composition of the solution depending on the chemical nature of the material. This provides yet another reason to perform snow analyses immediately upon melting.

Acid Meltout

Several snow researchers (Siep, 1978; Hagen and Langeland, 1975) have discovered that during the first stages of melt an acidic solution drains from the snowpack. Attempting to verify this phenomena in the Colorado study area, the research team conducted a single experiment in November of 1982 using snow obtained from Cameron Pass. Two 5-gallon containers were filled with snow from an area just north of Cameron Pass (See Figure 25). The snow was cut into cylindrical sizes which would fit into the sample containers without disturbing the snow structure (See Figure 28). The containers were able to hold the entire depth of snow at this sampling site due to the shallow 18-inch snowpack. These were transported directly to the laboratory and stored in a freezer. On November 5, 1982, the first sample was removed and exposed to a 60-watt light source focused on the snow surface. Melt-water was collected as it drained through an opening in the bottom of the container (See Figure 29). The pH was measured sequentially in volumes of 100 ml meltwater. Table 7 shows the results.

As can be seen from Table 7, a slightly acid trend is present, beginning with samples 6-18 and ending with more basic samples 19-28. A greater acid "flush" would have been expected if the phenomena mentioned earlier was controlling this meltout.

A second container was removed on November 19, 1982, from storage and melted producing similar results, perhaps having a tendency towards acid melt in the middle samples (See Table 8).

The lack of any drastic pH drop in the first stages of melt is not surprising. The relative purity of the sampled snow may be preventing a significant brine buildup in the melt. More investigation examining



Figure 28. Field sampling of snow for experiment meltout, Cameron Pass, Colorado, 1982.

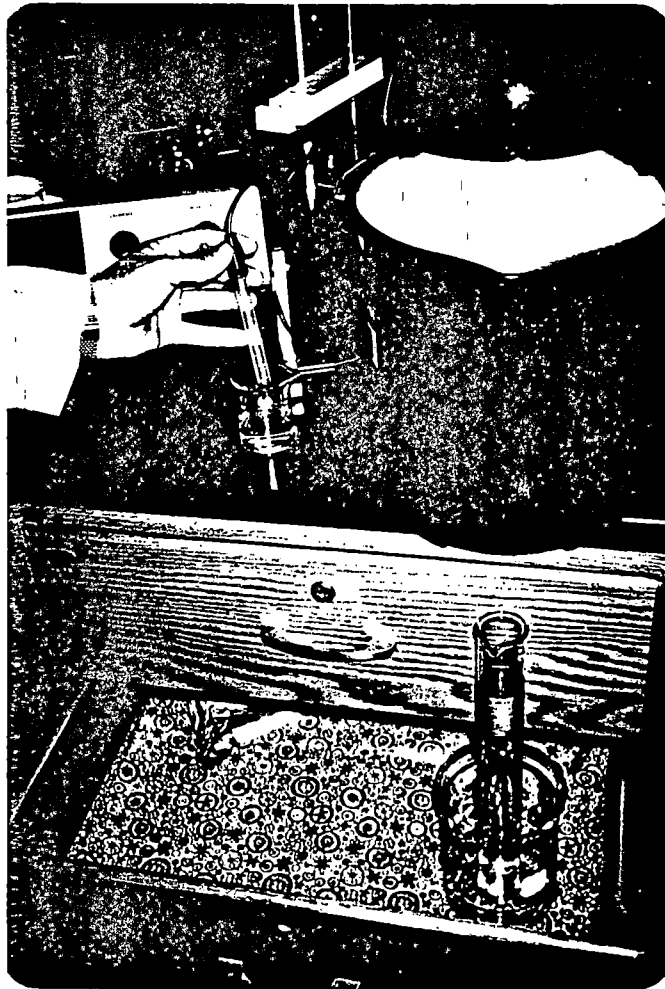


Figure 29. Laboratory arrangement for experiment meltout, 1982.

Table 7. Sequential pH measurements of snow obtained on October 31, 1982, from Cameron Pass, Colorado, and used in experiment meltout. Run number 1. Volumes for each sample were 100 ml.

Sample No.	pH	Sample No.	pH	Sample No.	pH
1	5.41	11	5.20	21	5.51
2	5.34	12	5.25	22	5.54
3	5.29	13	5.31	23	5.59
4	5.41	14	5.37	24	5.64
5	5.70	15	5.31	25	5.51
6	5.24	16	5.32	26	5.61
7	5.25	17	5.37	27	5.48
8	4.54	18	5.09	28	6.00
9	5.14	19	5.42		
10	5.34	20	5.45		

a wide range of snow of varying purities would help to define the level of contamination where acid melt occurs.

The pH measurements are higher than that found in other samples taken on the same day and this is attributed to the increase in pH with time relationship discussed earlier. Future experiments of this nature will be conducted immediately after sampling and with varying qualities of snow.

Measurements of Acidity

If we wish to determine the source of contamination at a particular site, we must first check the quality of snow around that site

Table 8. Sequential pH measurements of snow obtained on October 31, 1982, from Cameron Pass, Colorado, and used in experiment meltout. Run number 2. Volumes for each sample were 100 ml.

Sample No.	pH	Sample No.	pH	Sample No.	pH
1	5.79	11	5.72	21	5.12
2	5.65	12	5.55	22	5.03
3	6.20	13	5.65	23	5.00
4	6.25	14	5.50	24	5.31
5	6.05	15	5.21	25	5.45
6	5.72	16	5.24	26	5.74
7	5.88	17	5.22	27	5.58
8	5.49	18	5.25	28	5.05
9	5.21	19	5.61	29	6.21
10	5.33	20	5.24	30	6.12

to learn if the pollution is local or regional. If snow upwind is more contaminated than that found in town or below, we may have a distant source of pollution as is the case in many parts of Scandinavia. Should the snow be less contaminated in these upwind areas, we may have a local source of pollution as was suspected with many ski towns in the sub-alpine zone of Colorado. Finding the source requires a chemical analysis of the snow as well as a complete inventory of pollutants being emitted during the study period. This type of analysis was not possible due to the lack of air resource data at Vail and Telluride. The research team, however, did investigate further the background levels of acidity (quantitative capacity to react with a strong base to a designated endpoint pH) within the mountain snowpack.

This was carried out at three sites located near Cameron Pass (See Figure 25). The importance of using acidity as a measure of the potential hazard to water resources must be understood. Although fresh snow may have pH values as low as 4.4, the amount of acidity within the snow is actually very small when compared to the buffering capacity of most soils and vegetative cover. As a result, runoff from this acidic snow is not expected to cause serious damage to water resources unless it has avoided contact with a buffering material. This may be true in areas where soils are poorly developed and runoff is rapid, as is the case in many alpine watersheds. By sampling at Cameron Pass the research team was able to measure the acidity and pH of the entire snow-pack at a variety of locations and examine pH once more in a wilderness setting. Since most pH values in Vail, Telluride, and Keystone were typically higher than what would be expected (pH 5.6-5.8), and most pH values at Flat Tops and American Lakes were lower than expected, the research team conducted another investigation to determine what acidification of snow exists in the remote and vulnerable alpine watershed systems.

At each of three sites at Cameron Pass duplicate samples were obtained using a Federal Sampler to extract several cores as snow from the surface to the ground (See Figures 25 and 30). Results are shown in Table 9.

At site 1, three cores were taken to fill one container, four at site 2, and six at site 3. In each case, sample "b" was obtained several meters away from sample "a". Table 10 shows pH measurements at each of the three sites in increments of six inches. These were obtained by inserting a plastic graduated cylinder into a snow pit



Figure 30. Sampling for acidity at Cameron Pass, Colorado, 1983.

Table 9. Integrated pH measurements of snow obtained at Cameron Pass, Colorado, February 6, 1983, using a Federal Sampler.

Site/Location		pH
Site 1 - Zimmerman Lake	a.	5.09
	b.	5.06
Site 2 - West Cameron Pass	a.	5.14
	b.	5.18
Site 3 - Chambers Lake	a.	5.19
	b.	5.16

wall and extracting a core of sufficient size to make laboratory measurements (See Figure 31). By measuring pH with depth as uniform increments, any flow of acid melt within the snowpack could be detected as well as pH variability as a function of depth or storm event. Due to time constraints, a complete stratigraphic analysis correlated with pH was not attempted, though future research will attempt to do so. What was discovered was the high variability of pH with depth and perhaps storm event. This kind of variability cannot be due to acid migration through the snowpack. Every layer sampled contained no free water or significant ice formations indicative of melting. Variable pH measurements at each of the three sites can be attributed to snow either falling at variable pH's and becoming incorporated into the snowpack or snow falling at relatively uniform pH's and changing due to mechanisms such as dryfall or washout previously discussed in Chapter 1.

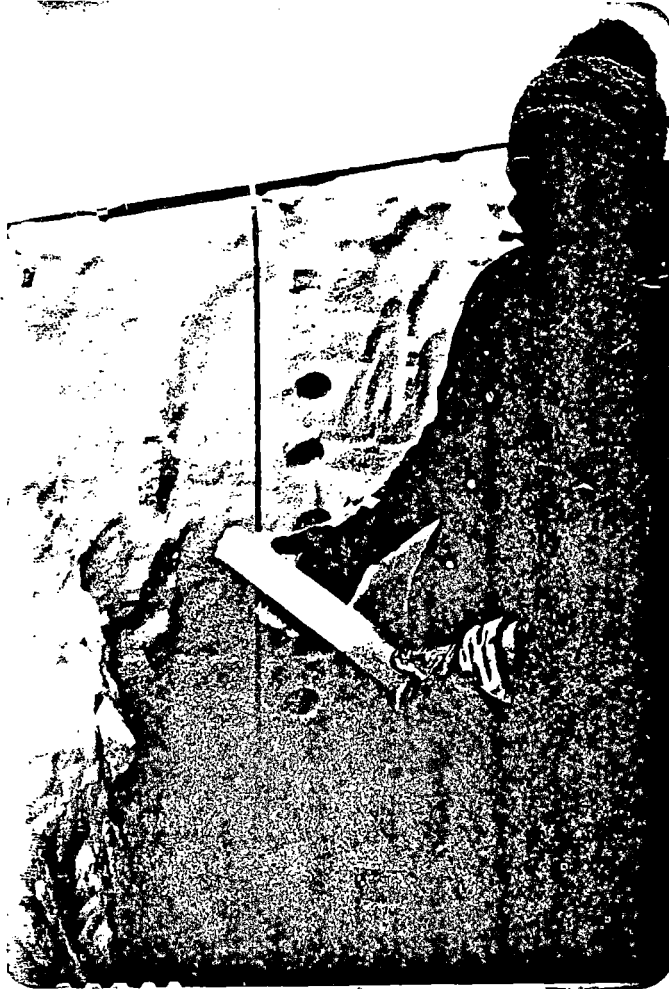


Figure 31. Extraction of snow cores in a snow pit, Cameron Pass, Colorado, 1983.

Table 10. pH measurements with depth obtained at sites 1, 2, and 3, Cameron Pass, Colorado, February 6, 1983.

Site	Depth (from surface) inches	pH
1	6 inches	5.28
	12 inches	5.32
	18 inches	5.41
	24 inches	5.32
	30 inches	5.57
	36 inches	5.64
	42 inches	5.13
	48 inches	5.09
	54 inches	5.11
	60 inches	6.44
	Total Depth: 62 inches	
2	6 inches	5.26
	12 inches	5.18
	18 inches	5.57
	24 inches	5.35
	30 inches	4.86
	36 inches	5.23
	42 inches	5.25
	48 inches	5.68
	Total Depth: 50 inches	
3	6 inches	4.68
	12 inches	5.68
	18 inches	4.91
	Total Depth: 18 inches	

The pH measurements for site 1 in Table 10 are generally higher than the core pH of 5.06 to 5.09. This may be due to the relative influences of each layer of snow within the snowpack on pH. The lower layers tended to be more dense (250 to 300 Kg/m³) and thus contributed far more to the total pH than the surface layers which had densities less than 100 Kg/m³. In addition, cores were obtained several meters away from the snow pit (to avoid collapse of the wall) and may have a slightly different snow composition than that found within the pit. Sites 2 and 3 have fair agreement when comparing the mean pH of six-inch measurements and the core pH.

The acidity of snow at these three sites was measured from samples obtained by coring. Titrations were carried out using an 0.2 N solution of NaOH to a pH endpoint of 8.3. Table 11 shows acidity in mg CaCO₃/L. The acidities ranged from 18 to 27 mg CaCO₃/L which is considered low when keeping in mind the high buffering capacities of soil and vegetation. What may be of concern is the high alpine region mentioned earlier and studied by Turk and Adams (1983). They reported alkalinities (quantitative capacity to react with a strong acid to a designated pH) as low as 3.5 mg CaCO₃/L titrating to a pH of 4.5. Should acidity values increase to levels higher than that reported, acidification may begin in lakes with low buffering capacities.

Periodic monitoring of the alpine snowpack would be necessary to identify trends which may lead to the buffering capacities of these lakes being exceeded and result in a rapid pH change towards a more acidic and less desirable aquatic habitat. By identifying lakes with the least alkalinity and measuring acidity of snowpack in late

Table 11. Acidity of snow samples obtained at Cameron Pass, Colorado, sites 1, 2, and 3, on February 6, 1983, expressed as mg CaCO_3/L to an endpoint of pH 8.30.

Site	mg CaCO_3/L
Site 1-a	27 mg CaCO_3/L to pH 8.30
1-b	21 mg CaCO_3/L to pH 8.30
Site 2-a	19 mg CaCO_3/L to pH 8.30
2-b	18 mg CaCO_3/L to pH 8.30
Site 3-a	22 mg CaCO_3/L to pH 8.30
3-b	25 mg CaCO_3/L to pH 8.30

winter around these lakes, we could quantitatively estimate the degree of pH change. This method of monitoring would take into account the variations in buffering capacities of different lakes and also the yearly variation in acidity found within the snowpack. No other system at this time can provide the site specific information necessary to evaluate the hazards to alpine water resources from contaminated snow.

Another subject investigated at Cameron Pass was the mechanism involved in polluting the snow. Two mechanisms were suspected to be contaminating the Rocky Mountain snowpack:

- 1.) Washout/rainout (resulting in contaminated initial layers of snow and cleaner upper layers from the same event).
- 2.) Dry deposition (resulting in uncontaminated initial layers of snow and having a contaminated surface layer).

Cores were removed in 2½ inch increments from the top 10 inches of the snowpack at sites 1 and 2 and from the top 5 inches of the snowpack at site 3 (See Figure 32). Sites 1 and 2 had approximately 12 inches of new snow, and site 3 had no new snow. The pH values with depth are shown in Table 12.

Table 12. pH values of snow from Cameron Pass, Colorado, February 6, 1983.

Site	Depth (inches)	pH
1	0.0 inches to 2.5 inches	5.05
	2.5 inches to 5.0 inches	5.16
	5.0 inches to 7.5 inches	5.14
	7.5 inches to 10.0 inches	5.32
2	0.0 inches to 2.5 inches	5.18
	2.5 inches to 5.0 inches	5.02
	5.0 inches to 7.5 inches	4.98
	7.5 inches to 10.0 inches	5.34
3	0.0 inches to 2.5 inches	4.59
	2.5 inches to 5.0 inches	4.83

As seen in Table 12 the pH of fresh snow shows decreasing values at site 1 and increasing values at site 2 when viewed from the deepest deposit upward. Site 3 shows snow at the surface having a pH of 4.59 with less contamination beneath it which may mean dryfall has influenced the pH. Both processes may have a relative influence on the pH of single event snowfalls and need to be investigated using



Figure 32. Extraction of cores from fresh snow,
Cameron Pass, Colorado, 1983.

a greater number of samples than those obtained from the three sites at Cameron Pass. The logistical problems, however, of digging enough snow pits and obtaining enough cores of snow prior to more snow falling or present snow melting to obtain a desirable number of samples should be noted. This information will be incorporated into the design of future experiments.

On March 18, 1983, the research team attempted one final experiment to further determine the pH and acidity of the mature northern Colorado snowpack. Three sites were originally selected to be sampled. These were Rabbit Ears Pass, Cameron Pass, and Willow Creek Pass, though Willow Creek Pass was abandoned due to road closure at the time of sampling (See Figure 1). At Cameron Pass and Rabbit Ears Pass, twenty and nineteen samples respectively were obtained in a transect with samples approximately 100 feet apart (See Figures 33 and 34). All were obtained in forested openings. A Federal Sampler was used to extract two full cores per container. This ensures a more representative sample knowing that sometimes a single core is not complete and thus would introduce error. Depth was recorded at each sample site. All samples were stored in Nalgene 1-gallon containers which had been rinsed with distilled water. They were transported to Colorado State University's Water Quality Laboratory and analyzed for pH and acidity as described earlier. Sample 22 at Rabbit Ears Pass was rejected due to its high moisture content. It had inadvertently been extracted from a depression containing free water, possibly a small stream. Its pH and acidity were indicative of water which has been buffered. All other samples contained little



Figure 33. Sampling site for acidity measurements,
Cameron Pass, Colorado, 03-18-83.

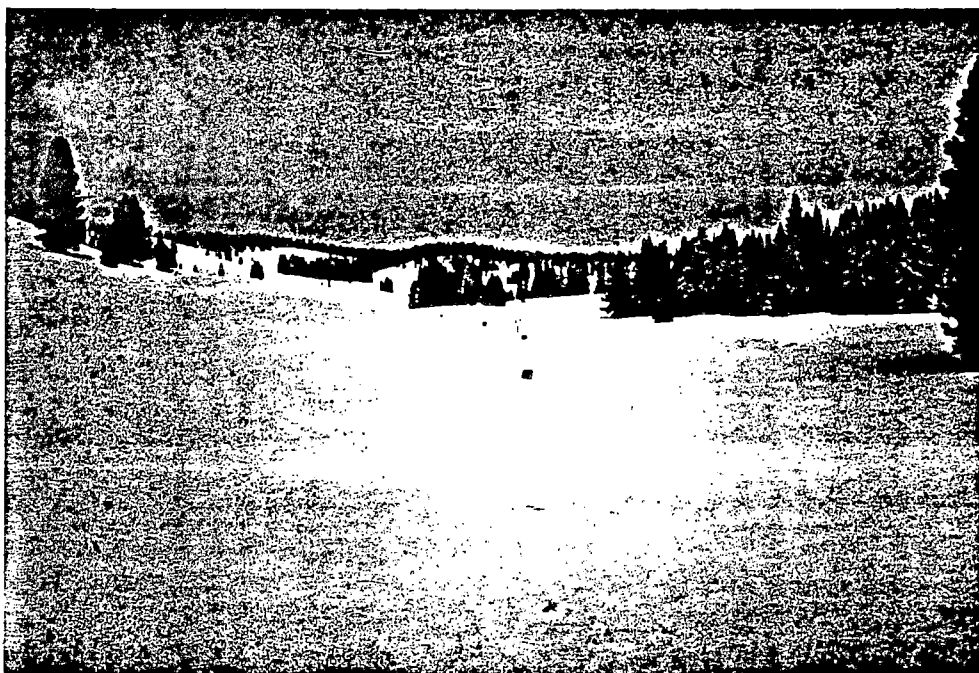


Figure 34. Sampling site for acidity measurements,
Rabbit Ears Pass, Colorado, 03-18-83.

Table 13. Analysis of snow samples from Cameron Pass, Colorado, March 18, 1983, including depth, pH, and acidity (mg CaCO_3/L titrated to a pH endpoint of 8.3 with .02 N NaOH).

Sample No.	Depth (inches)	pH	Acidity (mg CaCO_3/L)
1	90	5.1	17.5
2	82	5.0	16.7
3	86	5.0	18.6
4	70	5.1	16.1
5	63	4.9	17.5
6	75	5.0	15.9
7	100	5.1	16.6
8	95	5.0	15.9
9	88	5.0	15.7
10	70	5.0	15.3
11	82	5.0	15.3
12	79	5.1	17.0
13	67	5.1	17.2
14	90	5.0	17.1
15	90	5.0	15.9
16	86	5.0	18.6
17	83	4.9	17.8
18	78	5.2	15.2
19	90	5.2	14.1
20	71	4.9	17.8

geometric mean pH: 5.02

standard deviation: .07

pH range: 4.9-5.2

mean acidity: 16.55 mg CaCO_3/L

standard deviation: 1.17 mg CaCO_3/L

range: 14.1-18.6 mg CaCO_3/L

Table 14. Analysis of snow samples from Rabbit Ears Pass, Colorado, March 18, 1983, including depth, pH, and acidity (mg CaCO_3/L titrated to a pH endpoint of 8.3 with .02 N NaOH).

Sample No.	Depth (inches)	pH	Acidity (mg CaCO_3/L)
21	62	4.9	22.5
22	61	5.5*	16.0*
23	62	4.7	21.4
24	75	4.8	19.4
25	86	4.7	20.1
26	83	4.9	19.3
27	79	4.7	20.8
28	81	4.8	18.5
29	79	4.8	18.5
30	83	4.7	22.7
31	86	4.8	19.1
32	76	4.8	23.5
33	80	4.8	19.4
34	83	4.8	20.1
35	79	4.7	23.7
36	80	4.9	18.0
37	82	4.7	19.1
38	81	4.8	17.6
39	83	4.8	19.1

geometric mean pH: 4.78

standard deviation: .065

pH range: 4.7-4.9

mean acidity: 20.16 mg CaCO_3/L

standard deviation: 1.87 mg CaCO_3/L

range: 17.6-23.7 mg CaCO_3/L

*Sample 22 was inadvertently extracted from a depression in which free water had permeated through the snow. It was not included in the statistical analysis.

or no free water and were included in the statistical analysis.

Results are reported in Tables 13 and 14.

Statistical analysis revealed the two sites were distinctly different in terms of pH and acidity. Statistics of Cameron Pass snow samples were as follows:

mean geometric pH: 5.02
 standard deviation: .07
 pH range: 4.9-5.2
 mean acidity (mg CaCO_3 /L titrated to a pH endpoint of 8.3):
 16.55 mg CaCO_3 /L
 standard deviation: 1.17 mg CaCO_3 /L
 range: 14.1-18.6 mg CaCO_3 /L

Statistics of Rabbit Ears snow samples were as follows:

mean geometric pH: 4.78
 standard deviation: .065
 range: 4.7-4.9
 mean acidity (mg CaCO_3 /L titrated to a pH endpoint of 8.3):
 20.16 mg CaCO_3 /L
 standard deviation: 1.87 mg CaCO_3 /L
 range: 17.6-23.17 mg CaCO_3 /L

Although the differences in pH and acidity between these two sample sites is small, they are distinct. This is clearly illustrated by Figures 35 and 36. The possibility of snow at Rabbit Ears Pass being more acidic than snow at Cameron Pass due to its proximity to the Craig and Hayden, Colorado, coal fired power plants is a hypothesis worthy of further investigation by expanding snowpack analyses in locations radiating outward from these possible sources of snow contaminants.

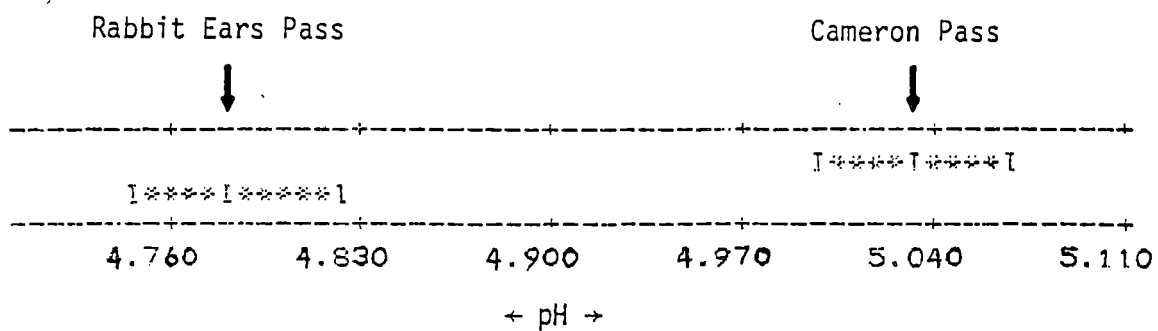
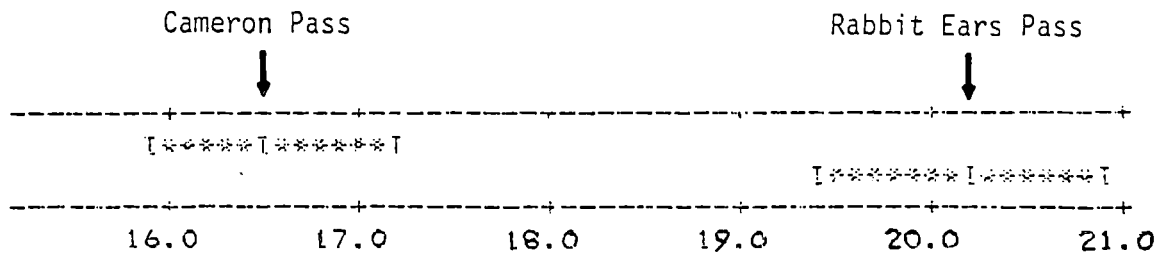


Figure 35. Individual 95 Percent Confidence Intervals for Level Means (based on pooled standard deviation) of pH values from Cameron Pass, Colorado, and Rabbit Ears Pass, Colorado. Snow samples obtained 03-18-83.



Acidity in mg CaCO_3 /L titrated to a pH endpoint of 8.3

Figure 36. Individual 95 Percent Confidence Intervals for Level Means (based on pooled standard deviation) of acidity values from Cameron Pass, Colorado, and Rabbit Ears Pass, Colorado. Snow samples obtained 03-18-83.

CHAPTER IV

SUMMARY AND CONCLUSIONS

This study was undertaken to determine the magnitude of snow acidification at selected sites in Colorado, including both areas of dense population, such as ski resorts, and areas of little or no population, such as wilderness areas. The study investigated snow pH and acidity over two winters and at six separate locations. The results are believed to be a first step towards examining snow acidification and it is hoped that through this research a better technique for evaluating resource damage due to acidic snow has evolved.

Based on field and laboratory measurements made from 1981 to 1983, the following results were obtained:

- 1.) The pH of snow in Colorado resort communities will vary between localities and between storm events by as much as 2 to 3 pH units.
- 2.) Differences in the pH of snow at sites within the same community is due to depositional patterns greatly influenced by local meteorological conditions.
- 3.) The pH values in snow within mountain communities will have greater concentrations of SO_4^- , NO_3^- , and Ca^{++} than snow from relatively uncontaminated wilderness areas, yet generally will be at or above the expected pH of 5.60 to 5.80.

- 4.) High pH values of snow in mountain communities are largely the result of Ca^{++} which is found in concentrations far exceeding that measured in remote or wilderness sites. This calcium is, therefore, from a local and anthropogenic source. Calcium appears to have a strong controlling effect on pH despite varying concentrations of other constituents.
- 5.) No adverse effects are expected on water resources below these communities as long as the calcium concentrations remain proportionately high enough to buffer any acidity due to sulfate or nitrate compounds.
- 6.) The pH of snow in remote sites, such as wilderness areas, is lower than expected (4.4 to 5.5). It contains enough $\text{SO}_4^{=}$ and NO_3^{-} contamination to be acidic only due to the lack of significant concentrations of buffering compounds such as CaCl_2 . The pH variability of recent snow-water within a medium-sized watershed is minimal (.1 to .2 pH units) when sampled in small openings of homogeneous vegetation, and measurements in the field showed no significant difference in pH when compared to measurements performed promptly in the laboratory.
- 7.) The pH measurements of snow must be obtained in exceptionally clean containers and stored in a frozen state. They should be analyzed as soon as possible upon returning to the laboratory. Duplicate samples should be taken at all sites. The pH measurements will change over time (rise), especially if the sample is exposed to air or unnecessarily shaken.

- 8.) Snow obtained in a wilderness area showed only a slight tendency to meltout an acid brine (thereby leaving less-acidic snow material behind). The minor effect of this phenomena is attributed to the lack of serious contamination in the Colorado snowpack.
- 9.) The measured acidity expressed in mg CaCO_3/L to an endpoint of pH 8.30 proved to be an excellent quantitative way of measuring the magnitude of acidity within the snow. By coring the mature winter snowpack, a realistic assessment of the strength of these acids can be obtained.
- 10.) Acidities were measured at Cameron Pass and Rabbit Ears Pass by extracting full snow cores (surface to ground). The acidity at Cameron Pass ranged from 14.1 to 18.6 mg CaCO_3/L , had a mean acidity of 16.55 mg CaCO_3/L , and standard deviation of 1.17. The pH ranged from 4.9 to 5.2, had a geometric mean of 5.02, and standard deviation of .07. The acidity at Rabbit Ears Pass ranged from 17.6 to 23.7 mg CaCO_3/L , had a mean acidity of 20.16 mg CaCO_3/L , and standard deviation of 1.87. The pH ranged from 4.7 to 4.9, had a geometric mean of 4.78, and standard deviation of .065. Snow from Cameron Pass was distinctly less acidic and had a higher pH than snow obtained from Rabbit Ears Pass.

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